TECHNOLOGY DEPT.

R.R.

ANALYTICAL ABSTRACTS

Dealing with all branches of Analytical Chemistry: Published Monthly with THE ANALYST by the Society for Analytical Chemistry

PUBLIC LIBRARY
JUL 8 1954
DETROIT

Editor: NORMAN EVERS, B.Sc., Ph.D., F.R.I.C.
20, EASTCHEAP, LONDON, E.C.3
Telephone: MANsion House 6608

Published for the Society by
W. HEFFER & SONS, LTD., CAMBRIDGE, ENGLAND

Volume 1 Price 4s.
Subscription Rate, inclusive of Index, 50s. per annum, Post Free
No. 6, Abstracts 1176-1440 June, 1954

BIBLIOGRAPHY OF STANDARD TENTATIVE AND RECOMMENDED OR RECOGNISED METHODS OF ANALYSIS

Compiled under the authority of the
Analytical Methods Committee of the Society of Public Analysts and Other Analytical Chemists
by
The Standard Methods Sub-Committee

Bound in rexine **25s.** net (available to members of the Society at a reduced price upon direct application to the Secretary, The Society for Analytical Chemistry, 7-8, Idol Lane, London, E.C.3).

This unique guide to the literature of analytical methods consists of annotated references to a very wide range of subjects. The text is divided into 33 subject groups; the classification is based on that used in *British Abstracts*.

Published for the Society by

W. HEFFER & SONS LTD., CAMBRIDGE

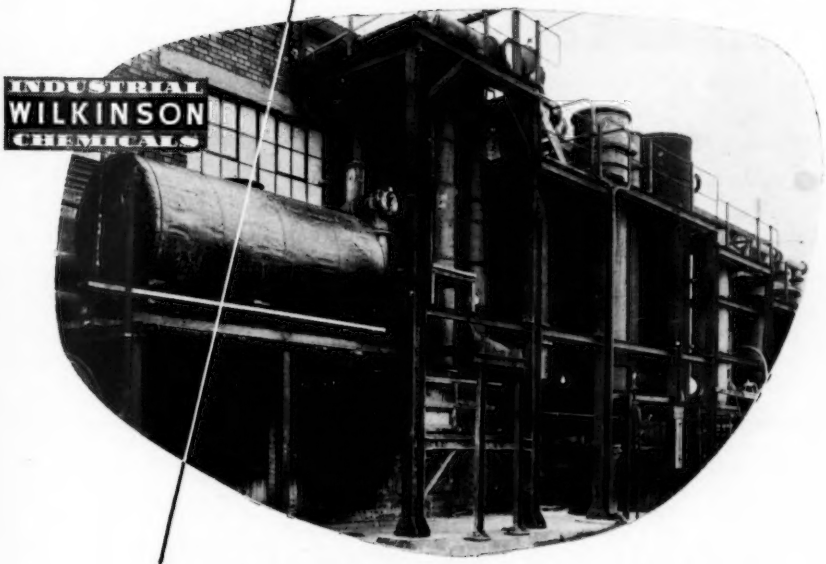
PRICE OF ANALYTICAL ABSTRACTS

Subscription Rate, inclusive of Index	50s. per annum, post free.
Abstracts printed on one side of the page only, exclusive of Index	60s. per annum, post free.

The subscription rate for *The Analyst* together with *Analytical Abstracts* and Indexes is 80s. per annum, post free.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 7-8, Idol Lane, London, E.C.3. Telephone: MANsion House 6608.

REAGENT QUALITY CHEMICALS



HYDROFLUORIC ACID 40% & 48%
SULPHURIC
HYDROCHLORIC
AMMONIA NITRIC

Also Technical Quality Fluorides for Industry and Research

JAMES WILKINSON
AND SON LIMITED
TINSLEY PARK ROAD · SHEFFIELD 9
PHONE:– 41208 (3 LINES) GRAMS:–"CHEMICALS SHEFFIELD"

Available from stock

Sodium tetraphenylboron
Lithium aluminium hydride
Sodium borohydride
Potassium borohydride
Lithium borohydride
Chloranilic acid
Naphthoresorcinol
Digitonin - α,α′-Dipyridyl

and over 2000 other organic research chemicals

L. LIGHT & Co. Ltd.
Colnbrook · Slough · Bucks

ALWAYS ASK FOR

WHATMAN
FILTER PAPERS

and ensure absolute accuracy in your analytical tests

THE RANGE OF WHATMAN FILTER PAPERS NOW MANUFACTURED COVERS EVERY LABORATORY FILTRATION AND CHROMATOGRAPHIC WORK

Made by:—
W. & R. BALSTON LTD., MAIDSTONE, KENT

Sole Sales Agents:—
H. REEVE ANGEL & CO., LTD.,
BRIDEWELL PLACE, E.C.4.

HEFFER'S of CAMBRIDGE

publish from time to time catalogues and lists of books in various subjects, and announcements of individual new books of special importance. Let us add your name to our mailing list

W. HEFFER & SONS, LIMITED

3 & 4 PETTY CURY, CAMBRIDGE

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1176. **Rapid analysis: semi-automatic dilution methods for economy of time and material.** E. Dannenberg (*Anal. Chim. Acta*, 1954, **10** [3], 237–242).—Dilutions commonly made by measuring calculated volumes of soln. and diluting with water in a calibrated flask can be more conveniently effected by taking a standard vol. of soln. in a pipette and adding the required vol. of water. A dilution table is provided, and a number of applications, drawn largely from clinical practice, are quoted. W. C. JOHNSON

1177. **Analytical value of exchange reactions between soluble and slightly soluble electrolytes.** O. R. Gottlieb (*Anal. Chim. Acta*, 1954, **10** [3], 222–236).—Reactions are described for the identification of anions in solution by their reactions with slightly soluble electrolytes. When 1 drop of a neutral soln. of an oxalate ($<$ 1:20,000) or a fluoride ($<$ 1:10,000) is added to a little calcium carbonate previously moistened with phenolphthalein soln. a red colour is produced. The following anions react similarly with the solids named and the figures indicate the sensitivity limits. With barium carbonate: SO_4'', 1:25,000; CrO_4'', 1:16,000. With lead carbonate: CrO_4'', 1:10,000; PO_4''', 1:5000. With silver carbonate: Cl′, 1:50,000; Br′, 1:50,000; I′, 1:50,000; PO_4''', 1:6250. Silver thiocyanate moistened with acid ferric sulphate soln. yields a red colour with Br′, 1:250,000, and I′, 1:250,000. Silver thiocyanate alone gives an immediate darkening with Br′ (1:10,000) when exposed to diffused light. Lead iodate is mixed with a drop of the neutral test soln. and the liquid is then absorbed on a filter-paper; the moist spot is treated with 1 drop of 50 per cent. aq. KI and 1 drop of 3 *N* H_2SO_4: liberation of I indicates PO_4''', 1:50,000, or oxalate, 1:50,000. Silver iodate similarly used, but with slightly acidified (H_2SO_4) soln., gives reactions with Cl′, 1:100,000; Br′, 1:100,000 and I′: 165,000. The tests are subject to numerous interferences. The theory of the methods is discussed. W. C. JOHNSON

1178. **Nature of the so-called "molecular weight increase" effect.** K. B. Yatsimirsky (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 314–230).—The effect (Feigl, *Microchemie*, 1924, **2**, 186) on the sensitivity of a pptn. reaction of increase in the mol. wt. of the precipitant has been studied. From published data it is shown that the substitution for the H in the CH· group of various groups leads to changes in solubility which can be characterised for each group by a const. in the form of an increment, $\Delta \log S$; the average value for the hydroxyl group is 1·5, corresponding to a thirty-fold increase in solubility. G. S. SMITH

1179. **Micro-method for measuring reaction rates in solution under moderate pressures.** Thomas Rees (*Anal. Chem.*, 1954, **26** [1], 226–229).—Rapid heat transfer and easy temp. control are achieved by the use of glass melting-point capillaries as the reaction vessels for measuring rates of reaction in soln. The sealed capillaries will withstand pressures of 71 atm. or more. The method was applied to the reaction of acetic acid with aniline The rate constants, expressed in mole fractions and $min.^{-1}$, are 0·0767 $\pm$ 0·005 at 150°, 0·193 $\pm$ 0·013 at 175° and 0·392 $\pm$ 0·028 at 200° C. The activation energy is $\simeq$ 13,000 cal. per mole. G. P. COOK

1180. **Metal indicators. VII. The analytical application of an alkaline-earth-phthalein complex.** G. Anderegg, H. Flaschka, R. Sallmann and G. Schwarzenbach (*Helv. Chim. Acta*, 1954, **37** [1], 113–120).—A new substance called phthalein complexone formed by condensing cresolphthalein with formaldehyde and iminodiacetic acid is described. Complex formation with $Mg^{··}$, $Ca^{··}$, $Sr^{··}$, $Ba^{··}$ and $Zn^{··}$ has been investigated quant.; details of the absorption spectra are given. The use of this substance as an indicator for the titration of the alkaline earths is discussed; a method for the titration of SO_4'' is also given. D. LIFF

1181. **Rate of processes occurring during potentiometric titration.** L. Ya. Polyak and B. N. Kabanov (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 253–265).—The kinetics of the establishment of oxidation-reduction potentials in the system $Fe(CN)_6''' - H_2Fe(CN)_6''$ on a platinum electrode are studied from polarisation curves and from determinations of change of potential with time. The rate of the titration is governed by the slow rate of chemical reaction in the soln. and not by the rate of establishment of potential, which is rapid. In strongly acid soln. the reaction is—

$2H^{·} + Fe(CN)_6''' + e \rightarrow H_2Fe(CN)_6''$, and not $Fe(CN)_6''' + e \rightarrow Fe(CN)_6''''$.

The electrode potential is determined by the equation—

$$\epsilon = \epsilon_0 + \frac{RT}{F} \log \frac{[Fe(CN)_6'''][H^{·}]^2}{[H_2Fe(CN)_6'']}$$

The reaction is accelerated by $H^{·}$ and $K^{·}$. $Al^{···}$ does not render the platinum electrode insensitive, as is usually supposed, but interferes with the titration through formation of only slightly dissociated Al ferrocyanide. G. S. SMITH

1182. **Mechanism of high-frequency titration.** S. Fujiwara and S. Hayashi (*Anal. Chem.*, 1954, **26** [1], 239–241).—The resonance of HCl, NaOH, acetic acid, NaCl and HCl-NaCl solutions at various concn., and the change of resonance in the titration of HCl with NaOH for 4 acid concn. (*i.e.*, at 4 different resonance sensitivities) are measured in a high-frequency (2·54 or 5·98 Mc.p.s.) field. D. A. PANTONY

1183. **Addition agents in analytical precipitations.** R. B. Fischer and T. B. Rhinehammer (*Anal. Chem.*, 1954, **26** [1], 244–246).—The effect of various amounts of 42 substances on crystal morphology, speed of flocculation, co-precipitation and light sensitivity in the precipitation of $BaSO_4$, AgCl and Ni dimethylglyoxime is investigated. Thirteen of the substances improve $BaSO_4$ crystal size, some increase flocculation rate of AgCl, and naphthol yellow retards photolytic decomposition, but none has any effect on the precipitation of Ni dimethylglyoxime. Co-precipitation is not affected.

D. A. PANTONY

1184. **Contributions to fluorimetry. I. The dependence of intensity of fluorescence on dilution. Beer's law of light absorption confirmed by an indirect method for solutions at great dilution.** J. Eisenbrand (*Z. anal. Chem.*, 1953, **140** [6], 401–416).—A modified Pulfrich photometer suitable for quant. measurement of fluorescence is described. The relation between absorption spectra and fluorescent spectra is discussed from a practical and theoretical standpoint. The equation $F_1c_2 = F_2c_1$ is derived from Beer's Law, where F_1 and F_2 are the fluorescence intensities at concentrations c_1 and c_2, respectively. Hence Beer's Law is confirmed even at great dilutions. The minimum amounts of some compounds that can be detected by their fluorescence are listed.

P. S. STROSS

1185. **Flow and distribution of solutions in filter-paper. Influence in paper chromatography.** S. E. Wood and H. H. Strain (*Anal. Chem.*, 1954, **26** [2], 260–264).—The flow and distribution of water and soln. in paper have been investigated in order to place paper chromatography on a more quant. basis. The following conditions for dry and moist papers are investigated quant.: (*i*) upward flow in vertical strips, (*ii*) downward flow in vertical strips and (*iii*) radial flow in horizontal sheets. Migration rates are discussed for H_2O, H_2O and methyl orange, and H_2O and lactic acid saturated with methyl orange.

J. DAVIS

1186. **Electrochromatographic sequences.** T. R. Sato, W. P. Norris and H. H. Strain (*Anal. Chem.*, 1954, **26** [2], 267–271).—Relative migration rates of various cations are determined, the sequence providing a basis for their detection. Separation is based on one-way migration and continuous electrochromatography. The sequence depends on the properties of the cations, nature of the electrolyte soln. and sorption of ions by paper. The direction of migration can be reversed by complex formation. Knowledge of the electrochromatographic sequences provides a basis for the detection of various cations and makes possible new analytical separations.

J. DAVIS

1187. **Modified technique for paper circle chromatography.** E. Schwerdtfeger (*Naturwissenschaften*, 1953, **40** [6], 201).—Particulars of the modified technique are best followed by examining the illustrations provided. The advantages claimed are that during the course of the analysis several different fractions can be obtained by withdrawing a paper circle and replacing it by a fresh one at stated intervals. Hence a 10 min. fraction may withdraw leucine, phenylalanine, methionine, valine and tyrosine, whilst subsequently removed circles contain amino-acids with smaller R_F values.

P. HAAS

1188. **Versatile technique of paper chromatography.** F. Irreverre and W. Martin (*Anal. Chem.*, 1954, **26** [2], 257–260).—A system of wicks is used to vary and regulate the flow of solvent. Resolution is increased by causing the spots to travel any distance along the entire length of the paper. The chromatographic process may be continued after the solvent front reaches the end of the paper or may be stopped at any time. The technique yields reproducible chromatograms and allows a wide choice of working conditions. The over-all height of the all-glass apparatus is 18 in.

J. DAVIS

1189. **Use of infra-red radiation for detection of colourless substances on paper chromatograms.** D. R. Kalkwarf and A. A. Frost (*Anal. Chem.*, 1954, **26** [1], 191–195).—An instrument for recording infra-red emission or transmission of paper strips is described. The i.r. radiation of a developed paper chromatogram is compared with that of plain filter-paper, a section of the paper strip being exposed on one side to a heating mantle and the radiation transmitted or emitted by the other side being measured by a bolometer. It is possible to detect milligram amounts of a variety of colourless substances without the aid of a spectrophotometer.

G. P. COOK

1190. **Multiple-colour development method for use in paper chromatography.** C. C. Woodward and G. S. Rabideau (*Anal. Chem.*, 1954, **26** [1], 248).—A method is described for the detection of amino-acids, organic acids and sugars by the use, in sequence, of three colour developing indicators. Amino-acids are detected by application of 0·2 per cent. ninhydrin in water-saturated *n*-butanol, and organic acids by application of 0·1 per cent. of methyl red in ethanol; 3:5-dinitrosalicylate reagent is used for the identification of sugars. The limits of detection are 1 to 5 μg for amino-acids, $\simeq$ 25 μg for organic acids, 15 μg for reducing sugars and 60 μg for non-reducing sugars.

G. P. COOK

1191. **Precipitation chromatography on paper [impregnated] with inorganic ions. I.** M. Milone, G. Cetini and F. Ricca (*Ann. Chim., Roma*, 1953, **43** [10], 652–658).—A chromatographic type of separation of various cations by diffusing a solution containing them up strips of paper impregnated with precipitants such as Na_2SiO_3, Na_2AsO_3,$Na_2H_2Sb_2O_7$ or borax, with subsequent development by immersion in distilled water, can be effected. The order of precipitation of the ions by the various precipitants and the variation in length of the zone is occupied by each with its initial concentration is determined.

R. C. MURRAY

1192. **Precipitation chromatography by diffusion of inorganic ions into gels. II.** M. Milone, G. Cetini and F. Ricca (*Ann. Chim., Roma*, 1953, **43** [10], 659–669).—A quantitative study of the chromatographic separation of Hg^{I}, Pb^{II}, Cu^{II}, Cd, Fe^{III}, Al, Zn, Mn^{II}, Co^{II} and Ni^{II}, by banded precipitation in gelatin gels containing K_2HPO_4, Na_2AsO_3,Na_2SiO_3 and borax is described. The order of precipitation of the ions by the different precipitants and the effects of concn. of reactants and gelatin and of temp. on the length of the clear zone between successive bands are studied.

R. C. MURRAY

1193. **Calculation of integrated intensities in spectrographic micro-analysis.** J. K. Hurwitz (*J. Opt. Soc. Amer.*, 1954, **44** [1], 30–34).—A theoretical treatment is given by which the change in integrated intensity occurring when a spark traverse is made across a region in which a very high concn. gradient exists can be calculated. Account is taken of the size of the sparked volume, the spectrograph and microphotometer slit lengths, and the ratio of the camera speed to the sample speed. There appear to be applications to the analysis of segregates in metals and alloys even when the sparked volume is considerably larger than the segregates.

B. S. COOPER

1194. **The effect of argon atmospheres on the intensity of certain spectral lines.** S. J. Adelstein and B. L. Vallee (*Spectrochim. Acta*, 1954, **6** [2], 134–138).—The line intensities of 28 metals were evaluated with argon and argon - helium mixtures as environments for the d.c. carbon arc; the concn. of the metals in a matrix of calcium carbonate and powdered graphite varied from 67 to 1·3 p.p.m. Many of the lines showed an enhancement in the presence of argon, especially those of the more volatile elements. Occasionally the use of an argon environment markedly increases the sensitivity of analysis with the d.c. arc.

E. HAYES

1195. **Polarisation curves as a basis for electrochemical methods of analysis.** G. Charlot (*Chim. Anal.*, 1954, **36** [3], 63–65).—The importance of a thorough understanding of the polarisation curves involved in a number of potentiometric and amperometric titrations is emphasised by a critical examination of the curves for the systems Fe^{II} - Fe^{III}, As^{III} - As^{V}, Mn^{VII} - Mn^{II}, and for the potentiometric estimation of Fe^{II} by means of $KMnO_4$.

W. J. BAKER

1196. **Method for calculation of photometric curves in the study of X-ray absorption band margins.** E. E. Vaynshteyn (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 311–313).—An application in the X-ray field of a method described by Kaiser (*Spectrochim. Acta*, 1948, **3**, 159).

G. S. SMITH

1197. **Acoustic methods for gas analysis.** L. E. Lawley (*Chem. & Ind.*, 1954, [8], 200–203).—The potential industrial applications of acoustic measurements of the velocity of sound in gases include the maintenance of a mixture of gases at constant proportions and indication of the presence of dangerous gases in enclosed spaces. Of the methods available, that depending upon measurement of the relative phase shift of the voltage at a microphone a given distance from the source of sound as the gas mixture varies has been adapted to industrial use. Apparatus proposed enables a comparison to be made of the relative times of traverse in one direction of the sinusoidal wave-forms across the zero axis.

M. TADMAN

2.—INORGANIC ANALYSIS

1198. **Potentiometric differentiation of certain inorganic cations.** C. W. Pifer, E. G. Wollish and M. Schmall (*Anal. Chem.*, 1954, **26** [1], 215–217).—Non-aqueous titrations, which have proved useful for differentiating certain organic bases, have been found suitable for inorganic bases such as alkali metals and ammonia. Na and K acetates have been successfully differentiated in a solvent mixture of glacial acetic acid and chloroform on titration with 0·1 *N* perchloric acid in 1:4-dioxan. Differentiation between K acetate, *n*-butylamine and pyridine is also possible. Potassium and ammonium acetates are the strongest bases in the proposed non-aqueous solvent, and Ba, Cd, Ca, Pb, Li, Mg, Ni, Ag, Na, Sr and Zn salts were all in a class having a basicity comparable with that of *n*-butylamine, but stronger than that of pyridine. Although differentiation between Na and K only is claimed in the text, good differential potentiometric curves are shown for ammonium and Li acetates, ammonium and Na acetates, and K and Li acetates. Full experimental details are given; a glass - calomel electrode system was used.

B. LAMB

1199. **Quantitative separation of inorganic ions by ion exchange on alginic acid.** H. Specker, M. Kuchtner and H. Hartkamp (*Z anal. Chem.*, 1954, **141** [1], 33–39).—The separation of metal cations by alginic acid exchange is described. Heavy metals can be removed from a soln. and SO_4'' can be determined gravimetrically in the eluate without interference. Cations can be quantitatively determined by titration of $H^{\cdot}$ liberated from the alginic acid. Binary separations of $Cu^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$, $Cu^{\cdot\cdot}$ and $Ni^{\cdot\cdot}$, $Cu^{\cdot\cdot}$ and $Zn^{\cdot\cdot}$ and ternary separations of $Fe^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$, and $Fe^{\cdot\cdot}$, $Cu^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ have been achieved with good results.

C. G. TAYLOR

1200. **Accuracy of determination of hydrogen peroxide by cerate oxidimetry.** E. C. Hurdis and H. Romeyn, jun. (*Anal. Chem.*, 1954, **26** [2], 320–325).—Results of a study reported indicated that the accuracy of the cerate - H_2O_2 titration compares favourably with that of an indirect absolute (gravimetric) method of H_2O_2 analysis. In the latter method (described) the O evolved from the H_2O_2 on decomposition is allowed to escape and the H_2O formed is retained in the apparatus; the wt. of O evolved is then determined simply by subtracting the wt. of residual H_2O from the original sample wt. The accuracy of the cerate - H_2O_2 titration was further substantiated by comparing cerate and permanganate titrations. Intercomparison between H_2O_2 titrations by several different standard cerate solutions indicated that the accuracy was not affected by changing cerate concn., by substituting sulphatocerate for nitratocerate, or by using reagent grade rather than primary reference standard grade cerate as antioxidant.

O. M. WHITTON

1201. **Hydrogen peroxide determination in the presence of chromate.** J. Rynasiewicz (*Anal. Chem.*, 1954, **26** [2], 355–358).—An ion-exchange resin, Amberlite IRA-400, in nearly neutral conditions, adsorbed and satisfactorily separated chromate from H_2O_2. The H_2O_2 can be subsequently determined colorimetrically by the pertitanic acid method. The effects of temp., pH and chromate concn. on the decomp. of H_2O_2 in Na_2CrO_4 solutions have been determined. Results indicate that the low recoveries of peroxide from 10^{-2} to 10^{-3} *M* Na_2CrO_4 can be ascribed to peroxide decomposition during analysis rather than to faulty analytical procedure.

O. M. WHITTON

1202. **Gravimetric determination of lithium.** V. E. Plyuschev and I. V. Shakhno (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 293–298).—Solubilities (per cent. w/w) at 25° C of LiCl, NaCl and KCl in *n*-propanol, which are at equilibrium after stirring

for 6 to 7 days, are 15·60, 0·019 and 0·008, respectively. LiCl can be determined in a mixture with NaCl and KCl by extraction with *n*-propanol saturated with dry HCl. G. S. SMITH

1203. **A rapid volumetric estimation of sodium.** A. Herzka (*Chem. & Ind.*, 1954, [8], 221).—The method differs from that of Hurka (*Mikrochemie*, 1942, **30**, 297) in that, after adding potassium pyroantimonate to ppt. the Na salt, the reactants are shaken for ½ min., filtered and titrated immediately instead of after 3 hours, the values obtained being accurate to within ± 0·5 per cent.; a complete determination takes 2 to 3 min. M. TADMAN

1204. **Determination of sodium monoxide in sodium. An addendum.** L. P. Pepkowitz, W. C. Judd and R. J. Downer (*Anal. Chem.*, 1954, **26** [1], 246).—An increase in precision in the mercury-extraction method (*cf. Brit. Abstr. C*, 1951, 161) by means of improved technique is claimed. D. A. PANTONY

1205. **Rapid volumetric determination of potassium with sodium tetraphenyl boron.** W. Rüdorff and H. Zannier (*Z. anal. Chem.*, 1953, **140** [1], 1–5).—Potassium is determined by pptg. it from 0·1 *N* HNO_3 or H_2SO_4 soln. as $KB(C_6H_5)_4$ with a known excess of $NaB(C_6H_5)_4$ and filtering off the ppt., which is made easily filterable by the addition of a few drops of an Al salt soln. A known excess of $AgNO_3$ is run into the filtrate to precipitate $AgB(C_6H_5)_4$. The excess of silver is estimated by Volhard's method. As little as 15 mg of K can be estimated with an accuracy of ± 0·1 mg in the presence of large quantities of Li, Na, alkaline earths, Al, Cr, Zn or PO_4'''. Fe is complexed with NaF. NH_4^+, Rb and Co interfere, as do anions that give a ppt. with Ag. The determination takes 7 to 10 min. P. S. STROSS

1206. **Flame-photometric determination of alkali and alkaline-earth elements in cast iron.** D. F. Kuemmel and H. L. Karl (*Anal. Chem.*, 1954, **26** [2], 386–391).—A flame-photometric method for simultaneously determining small quantities of Ca (0·001 to 0·060 per cent.), Mg (0·001 to 0·160 per cent.), Na (0·001 to 0·040 per cent.) and Li (0·0005 to 0·010 per cent.) in experimental cast irons is described. The sample is dissolved in HCl and the insoluble residue of C and SiO_2 is removed by filtration. Most of the Fe is extracted with ether. The aqueous extract, after removal of ether and insoluble matter, is compared on a flame photometer with suitable standards. As P suppresses the radiation of Ca, and to a lesser extent Mg, these standards were prepared to contain approximately the P content of the cast irons to be analysed. The method is quicker than classical gravimetric techniques, but comparable in accuracy and precision. Typical calibration curves are given for the four elements determined. O. M. WHITTON

1207. **Determination of cuprous and cupric ions from a solution of their mixture: application of citrate complex formation.** S. J. Quadir and M. H. Khundkar (*J. Indian Chem. Soc.*, 1953, **30** [12], 846–850).—In presence of excess of citrate ion, Cu^{I} is quant. oxidised by I to Cu^{II}, which is converted immediately to its citrate complex; on addition of HCl the complex is decomposed, and the Cu^{II} is estimated iodimetrically. The optimum quantities of citrate and acid are stated. A soln. containing Cu^{I} and Cu^{II} is assayed by addition of 2 mol. of citrate per mol. of total Cu and a known excess of I, with subsequent titration with thiosulphate; 0·5 ml of 6 *N* HCl is then added per ml of *M* citrate, and the total Cu is estimated in the usual way. Addition of 2 to 5 g of KCNS improves the sharpness of the final end-point. Both Cu^{I} and Cu^{II} can be determined within ± 1 per cent. The sample used for the test should contain < 0·125 g of Cu^{II} and < 0·150 g of total Cu. H. P. PAGET

1208. **The precipitation of copper with arsanilic acid.** A. Musil and R. Pietsch (*Z. anal. Chem.*, 1953, **140** [6], 421–426).—Arsanilic acid (*p*-aminophenylarsonic acid) gives insol. ppt. with a number of metals (*e.g.*, Cu, Fe, Mg, Ce), depending on the pH of the soln. The Cu-containing soln. is approx. neutralised and brought to pH 5·2 with acetate buffer. For every 50 mg of Cu, 20 ml of freshly prepared 0·5 *M* sodium arsanilate soln. (adjusted to pH 6·8) is added. The ppt. is filtered and washed. Then either the ppt. is immediately dissolved in 30 drops of a 25 per cent. v/v soln. of conc. aq. NH_3, and the soln. made up to 100 ml and titrated with disodium salt of ethylenediaminetetra-acetic acid, with a mixture of ammonium purpurate and sodium chloride (1 + 200) as indicator, or the ppt. is dried to constant weight at 150° C and weighed (1 mg of precipitate ≡ 0·2143 mg of Cu). P. S. STROSS

1209. **An alkalimetric method for the determination of copper, mercury and nickel.** G. Denk (*Z. anal. Chem.*, 1953, **140** [2], 103–109).—A titration procedure is described in which cupric salts (with the addition of Na_2SO_4), mercuric salts (with the addition of NaCl) and nickel salts can be titrated at the boiling point with 0·1 *N* NaOH. Free acid if present must be determined separately. At the end-point (*o*-cresolphthalein), the basic salt $CuSO_4.3\,Cu(OH)_2$, $Ni(OH)_2$ or HgO is formed. The error is ± 1 per cent. P. S. STROSS

1210. **The polarographic behaviour of some elements in concentrated calcium chloride solution. IV. The determination of metallic impurities in calcium metal.** G. F. Reynolds, H. I. Shalgosky and T. J. Webber (*Anal. Chim. Acta*, 1954, **10** [2], 192–200).—Previous papers have described the polarographic behaviour of Cu, Cr, Ni, Pb, Cd and Mn in 5 *M* $CaCl_2$ (*Brit. Abstr. C*, 1953, 497; *Anal. Abstr.*, 1954, **1**, 27 and 28). The pH range for Fe was found to be too narrow for routine work and was therefore not used. A table comparing the $E_{\frac{1}{4}}$ of the elements with the peak voltages is given. Two solutions of different pH have to be used: (*i*) pH 1 to 2, Cr and Ni coincide with Pb and (*ii*) pH 7·0 to 7·5 at which Cr and Ni are pptd. and Pb is determined. A correction for the contribution of Pb to the current values has to be made. As separation of Cr from Ni is impossible, the Ni was determined chemically. Details of the method and of preparation of calibration curves are given. The order of the concn. dealt with is 5 to 100 p.p.m. B. LAMB

1211. **Spectrophotometric titrations with ethylenediaminetetra-acetic acid. II. Determination of magnesium, calcium, zinc, cadmium, titanium and zirconium.** P. B. Sweetser and C. E. Bricker (*Anal. Chem.*, 1954, **26** [1], 195–199).—At constant pH, a graph of absorbancy of very dil. solutions of Mg^{++}, Ca^{++}, Zn^{++}, Cd^{++}, Zr^{++++} and Ti^{++++} plotted against volume of added ethylenediaminetetra-acetic acid (**I**) shows an abrupt change at the end-point.

Mg, Ca, Zn and Cd are determined by adjusting the vol. of soln. to 100 ml and the pH to 10, and the absorbancy of the soln. at 222 or 228 mμ is measured for successive additions of 0·001 or 0·013 *M* **I** reagent that has been standardised with Ca solutions of known strength in a similar procedure; the end-point is found from the graph of absorbancy plotted against vol. of titrant. In NaOH soln., addition of citric acid and KCN allows the determination of Ca in presence of Mg and of Cd in presence of Zn, respectively. Zr is determined by titration of an added known excess of ethylenediaminetetra-acetic acid with standard $Fe^{\cdots}$ in presence of salicylic acid at pH 4 and 520 mμ. Ti is determined similarly in presence of H_2O_2 at pH 1·9, or by direct titration at 450 mμ. In all determinations blank titrations are carried out. Ions that interfere either have large absorption maxima at the wavelengths of measurement (small absorptions do not interfere) or form chelates with the reagent. Errors are claimed to be ± 1 per cent. in all determinations.

D. A. PANTONY

1212. **Direct heterometric micro-determination of zinc with quinaldic [quinaldinic] acid in the presence of other metals.** M. Bobtelsky and L. Bihler (*Anal. Chim. Acta*, 1954, **10** [3], 260–264).—Solutions of Zn salts (0·001 to 0·005 *M*) are titrated with 0·02 *M* Na quinaldinate, the end-point being determined photometrically as the initial point of max. turbidity. The titration can be carried out in the presence of salts of Mg, Ca, Ba, $Mn^{\cdot\cdot}$, $Fe^{\cdots}$, Al, $Cr^{\cdots}$ or Cd. The max. error is ± 1 per cent. $Ni^{\cdot\cdot}$ and $Co^{\cdot\cdot}$ interfere with the pptn.

W. C. JOHNSON

1213. **Gravimetric determination of zinc as mercurithiocyanate.** F. Sierra and J. Hernández Cañavate (*An. Soc. Esp. Fís. Quím., B*, 1953, **49** [11], 687–692).—Conditions for the pptn. of $ZnHg(CNS)_4$ in a very pure and coarsely cryst. state are given. To a solution, which may be acid, of $ZnSO_4$ or $Zn(NO_3)_2$ (≮ 0·01 *N*) and 10 ml of 10 per cent. glycerol is slowly added 10 per cent. $Na_2Hg(CNS)_4$ (10 ml per 0·1 g of Zn) at just below the b.p. After cooling for 2 hr., the ppt. is filtered and washed with 20 ml of aq. $Na_2Hg(CNS)_4$ - NaCNS (1 per cent. of each) and then 15 ml of ethanol, and dried at 140° C.

D. P. YOUNG

1214. **Analytical uses of trithiocarbonic acid. VIII. Separation of zinc from manganese, iron and alkaline earths.** A. Musil and W. Pilz (*Z. anal. Chem.*, 1954, **141** [1], 19–23).—The Zn - trithiocarbonic acid complex can be precipitated from acetic acid soln. containing Mn, Fe and alkaline earths at controlled pH and can be determined by titrating the redissolved complex with ethylenediaminetetra-acetic acid. Cations in the filtrate are determined by the same titrimetric method. Results for Zn are accurate to within ± 0·3 per cent.

C. G. TAYLOR

1215. **Cadmium thiourea reineckate procedure.** C. L. Rulfs, E. P. Przybylowicz and C. E. Skinner (*Anal. Chem.*, 1954, **26** [2], 408–410).—A study of the short direct thiourea reineckate procedure for determining Cd is reported. Sn, Sb, Cu, Bi, Hg and Pb interfere but can be previously separated. Few other ions are harmful, and Cd can be separated directly by the technique from almost any quantity of Zn. The method is particularly attractive at the semi-micro level because of the favourable gravimetric factor. The accuracy is + 0·4 per cent. The character and reasons for the specificity of this precipitation have been examined.

O. M. WHITTON

1216. **Extraction of cations as salts of fatty acids. II. Analytical and chromatographic separation of beryllium from iron and aluminium.** S. Banerjee, A. K. Sundaram and H. D. Sharma (*Anal. Chim. Acta*, 1954, **10** [3], 256–259).—$Fe^{\cdots}$ and $Al^{\cdots}$ are extracted completely by chloroform from aq. solutions containing butyric acid, the conditions being the same as those for the extraction of $Be^{\cdot\cdot}$ (*Anal. Abstr.*, 1954, **1**, 25). $Be^{\cdot\cdot}$ can be extracted selectively if complexone II (a Na salt of ethylenediaminetetra-acetic acid) is added before the butyric acid. Chromatographic separation of $Be^{\cdot\cdot}$ from $Fe^{\cdots}$ and $Al^{\cdots}$ is effected by eluting with 5 per cent. butyric acid in ethyl acetate on a paper-pulp column. Interference from $PO_4^{\prime\prime\prime}$ is avoided by adding zirconyl chloride and sequestering the excess with complexone II.

W. C. JOHNSON

1217. **Indirect polarographic determination of aluminium in presence of ferric iron and calcium.** D. Lydersen (*Z. anal. Chem.*, 1953, **139** [6], 401–408).—The analysis consists in determining the total Al + Fe^{III}; Fe^{III} is determined separately and Al is found by difference. The wave of disodium ethylenediaminetetra-acetate (**I**) at pH 4·7 is lowered by complex formation with either Fe or Al. A technique is described in which standard **I** is titrated with Al or Fe at pH 4·7 in presence of 0·02 per cent. gelatin, the end-point being obtained by extrapolation of polarographic waves (0·05 V *vs.* the S.C.E.). When the concn. of **I** is $2·8 \times 10^{-4}$ *M* or less, errors due to presence of Ca do not exceed 1 per cent.

P. S. STROSS

1218. **Rapid photometric determination of aluminium, iron and titanium in clays and refractory materials.** O. Glemser, E. Raulf and K. Giesen (*Z. anal. Chem.*, 1954, **141** [2], 86–93).—The paper describes photometric procedures for the determination of Al, Fe and Ti in clays and refractory materials. The complete analysis occupies about 2 hr.

Sample preparation.—Decompose ≃ 0·5 g of sample in a Pt crucible with 25 ml of 40 per cent. HF and 2·5 ml of conc. H_2SO_4 and heat the mixture on a sand-bath until all the HF has volatilised. Fuse the residue with 3 g of potassium pyrosulphate until the melt begins to crystallise. Dissolve the residue in warm 0·1 *N* H_2SO_4, transfer the soln. to a 250-ml calibrated flask and make up to the mark with 0·1 *N* H_2SO_4. The soln. is used for subsequent determinations. *Determination of Al.* To 5 ml of the prepared soln. in a 250-ml flask, add with stirring: 1 drop of 80 per cent. thioglycollic acid, 13 ml of 0·5 per cent. Eriochrome cyanine soln., 50 ml of acetate buffer soln. (pH 3·8) and H_2O to vol. Measure the absorption after 40 min. at 530 mμ. The amount of Al is calculated from a previously prepared graph. *Determination of Fe.*—To 50 ml of prepared soln., add 2 ml of 10 per cent. NH_4Cl soln., 2 ml of 20 per cent. sulphosalicylic acid soln. and 4 ml of 10 per cent. aq. NH_3. Ten min. after diluting to 100 ml measure the absorption of the soln. at 445 mμ. *Determination of Ti.*—Mix 50 ml of prepared soln. with 1 ml of 30 per cent. H_2O_2 and make the vol up to 100 ml. After 10 min. measure the absorption at 445 mμ.

C. J. KEATTCH

1219. **Volumetric determination of indium with ethylenediaminetetra-acetic acid.** H. Flaschka and A. M. Amin (*Z. anal. Chem.*, 1953, **140** [1], 6–9).—To a neutral or slightly acid indium soln. add an excess of tartaric acid and adjust the pH to 8 to 10 with buffer (13·4 g of NH_4Cl and 88 ml of conc. aq. NH_3 to 250 ml). Eriochrome black T powder (0·25 per cent. in NaCl) is added until the soln. is distinctly red. Heat to boiling point, and titrate with 0·01 *M* disodium ethylenediaminetetra-acetate soln. to a blue colour. At the end-point the soln. should remain blue for ½ min. Alkali metals, Tl^{I}, Ag, As, Sb, Mo, W, CrO_4'' and Sn^{IV} do not interfere. In presence of chromate the colour is green at the end-point. If Hg, Cu, Cd, Zn, Co, Ni or Fe are present add an excess of HCN to the neutral soln. before adjusting the pH. Ferricyanide, if present, is reduced to ferrocyanide by hydroxylamine hydrochloride. The titration should be done in dil. soln. (0·001 *M* with respect to In). The alkaline earths, Mn, Pb, Al, Ti and Bi interfere and must not be present. P. S. Stross

1220. **Effect of hydrogen ion concentration on the formation of indium dithizonate.** K. E. Kleyner and L. V. Markova (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 279–285).—Extraction of In^{III} dithizonate by means of CCl_4 is most complete at pH 3·5 in unbuffered soln., and at pH 4 to 4·3 in acetate-buffered soln. Pd, Au, Pt, Ag and small amounts of Zn and Cd can be completely separated from In without the use of complex formers at pH < 2·5, and Cu and Hg at pH 1 to 2. G. S. Smith

1221. **Spectrographic determination of certain rare earths in stainless steels.** E. W. Spitz, J. R. Simmler, B. D. Field, K. H. Roberts and S. M. Tuthill (*Anal. Chem.*, 1954, **26** [2], 304–307).—A spectrographic method (with d.c. arc) for determining as little as 50 μg of rare-earths in a 1-g sample of steel is described. The major steel components, including most of the Cr, are first removed electrolytically at a mercury cathode. As much as possible of the remaining impurities, such as Ca and Al, are then removed chemically. The less than milligram amounts of Ce, La, Nd, and Pr remaining in soln are concentrated by pptn. with aq. NH_3 by use of Fe''' as carrier. The combined hydroxides are dissolved in a minimum of HCl, and U and NaCl are added to serve as the internal standard and as the spectroscopic buffer, respectively. Although no precision study was made, a statistical study of the recoveries tabulated permits the estimation of a coeff. of variation of ± 10 per cent. of the amount present for any individual rare-earth. O. M. Whitton

1222. **The separation of adjacent rare-earths with ethylenediaminetetra-acetic acid by elution from an ion-exchange resin.** F. H. Spedding, J. E. Powell and E. J. Wheelwright (*J. Amer. Chem. Soc.*, 1954, **76** [2], 612–613).—Preliminary tests show that a rapid method of separating individual rare-earths by means of ethylenediaminetetra-acetic acid (**I**) is possible. A soln. of Pr_6O_{11} and Nd_2O_3 in excess of HCl was adjusted to pH 5 with aq. NH_3 and passed through a column of Nalcite HCR so as to saturate it; the amount of rare-earth adsorbed was then determined. A second similar column with 30 per cent. more resin was saturated with Fe''' by a solution of $Fe(NO_3)_3$. Water was added to remove NH_4' and NO_3'. The bottom of the first column was connected to the top of the second, and the system was eluted with a soln. of the diammonium dihydrogen salt of **I** (10 g per litre adjusted to pH 8·04 with aq. NH_3). The flow rate was fixed at 50 ml per hr. and 200-ml fractions were collected and analysed. D. Liff

1223. **A chemical-spectrochemical method for the determination of rare-earth elements and thorium in cerium minerals.** H. J. Rose, jun., K. J. Murata and M. K. Carron (*Spectrochim. Acta*, 1954, **6** [2], 161–168).—Cerium is determined volumetrically by conversion to ceric sulphate and titration with $FeSO_4$. Thoria and the rare-earth hydroxides are pptd., and sufficient pure ceric oxide is added to the ignited ppt. to bring the ceria content up to 80 per cent. This mixture is then examined in the d.c. carbon arc for La, Pr, Nd, Sm, Gd, Yb and Th, the spectral lines of singly ionised Ce being used as an internal standard. Results obtained on known mixtures and also on natural minerals previously analysed by chemical methods are given; the max. deviation amounts to 8 per cent., and the coefficient of variation for a quadruplicate determination of any element does not exceed 5·0 per cent. E. Hayes

1224. **Study of silicosis. Determination of the free silica content of dust inhaled by workers.** M. L. H. Martin (*Chim. et Ind.*, 1954, **71** [1], 91–94).—Free SiO_2 in the atmosphere of foundries is found by determining colorimetrically the total SiO_2 (with ammonium molybdate), the Al (with aluminon) and the Fe (with *o*-phenanthroline), and then calculating the free SiO_2 from the equation—

$$\text{Free } SiO_2\% = \text{Total } SiO_2\% - \left(\frac{Al_2O_3\% \times 2}{102} + \frac{Fe_2O_3\% \times 200}{160}\right)60$$

The method is rapid and reasonably accurate and unlike direct chemical methods can be applied to the very small samples of dust usually available in practice. J. M. Jacobs

1225. **A polarographic study of titanium ethylenediaminetetra-acetate complexes.** R. L. Pecsok and E. F. Maverick (*J. Amer. Chem. Soc.*, 1954, **76** [2], 358–362).—Ti^{III} and Ti^{IV} in solutions of ethylenediaminetetra-acetate (H_4Y) give well-formed reversible polarographic waves. Below pH2, $E_{\frac{1}{4}}$ is independent of pH. Above pH 2·5, there is a linear relation that indicates that two H ions are involved in the reaction. As the pH is increased, the waves become more irreversible, the diffusion currents diminish and the solutions become colloidal. The diffusion current is a direct measure of the complex in the presence of excess either of Ti or of complex former. Measurements of Ti, total complexing agent and diffusion current indicate that below pH 2 the electrode reaction is $TiY + e' = TiY'$; from pH 2·5 to 8 the reaction is $TiOY'' + 2H^{\cdot} + e' = TiY' + H_2O$. The following equilibrium constants have been determined: for $TiY' = Ti''' + Y''''$, 5×10^{-22}; for $TiOY'' = TiO^{\cdot\cdot} + Y''''$, 5×10^{-18}; for $TiY + H_2O = TiO^{\cdot\cdot} + 2H^{\cdot} + Y''''$, 3×10^{-23}; for $TiO^{\cdot\cdot} + H_2O = TiO_2 + 2H^{\cdot}$, 10^{-4}. Zinc as Zn acetate has no effect, but when added as $ZnCl_2$, the diffusion current increased non-reproducibly. Results were similar with SO_4''. With Zn the interference seemed mainly to be caused by the presence of Cl′. In this work therefore Cl′ and SO_4'' cannot be tolerated when the greatest accuracy is required. B. Lamb

1226. **The analytical chemistry of zirconium.** P. S. Murty and Bh. S. V. R. Rao (*Z. anal. Chem.*, 1954, **141** [2], 93–96).—The use of ammonium arsenate as a reagent for Zr is criticised because the presence of Th, Sn and Ti necessitate a double pptn., whilst W interferes in all proportions. Mandelic acid is a standard organic reagent for Zr, but suffers from the disadvantage that large amounts are needed for each determination. The authors recommend tetrachlorophthalic acid; it is said to be cheap, much less of it than mandelic acid is needed per determination and only large amounts of V necessitate a double pptn. As little as 0·5 mg of ZrO_2 can be determined and even 0·2 mg of ZrO_2 in 200 ml gives a distinct turbidity. *Procedure.*—A soln. containing 0·1 to 0·0005 g of ZrO_2 is treated with 20 ml of 50 per cent. NH_4NO_3 and 50 ml of 2 *N* HCl and the soln. is diluted to about 100 ml. After heating to boiling, 100 ml of a hot 1 per cent. tetrachlorophthalic acid soln. is added with stirring. The soln. is kept boiling for 2 min. The ppt. is filtered, washed with a hot soln. containing 2 per cent. of NH_4NO_3 and 0·1 per cent. of tetrachlorophthalic acid in 0·4 *N* HCl and finally with water. The ppt. is ignited to ZrO_2 and weighed. Free HCl can be tolerated up to a concn. of 0·6 *N*. The following elements do not interfere with the pptn.: Th^{++++}, Sn^{++++}, Sn^{++}, V^{++++}, Cr^{+++}, Fe^{+++} UO_2^{++}, Al, Ce-earths, Sb^{+++}, Ni, Co, Cu, Cd, Mn^{++}, Ca, Sr, Mg and Zn. Ti^{++++} interfere when present in quantities $> 1\frac{1}{2}$ times the amount of Zr. The structure of the Zr tetrachlorophthalate is briefly discussed.

C. J. KEATTCH

1227. **Phenylacetic acid: a new reagent for thorium.** A. Purushottam and Bh. S. V. R. Rao (*Z. anal. Chem.*, 1954, **141** [2], 97–100).—Phenylacetic acid is recommended as a reagent for Th. As little as 0·4 mg of ThO_2 can be determined. The pptn. is carried out as follows. To a measured volume of $Th(NO_3)_4$ in a beaker are added 10 to 15 g of NH_4Cl and the soln. is diluted to 150 ml with water. It is brought to the boil, and 150 ml of a hot 4 per cent. soln. of phenylacetic acid are added with continuous stirring. The resulting ppt. is filtered and, after washing and partially drying, it is ignited to the oxide. The pptn. of the Ce-earths can be prevented by the addition of up to 20 ml of a 0·1 *N* acid. However, high results are obtained when the amount of Ce-earths exceeds 4 times the amount of Th. Accurate results can be obtained by dissolving the ppt. in the min. quantity of 6 *N* HCl, neutralising the soln. to Congo red with aq. NH_3 and igniting the resulting ppt. Th can be determined in a Zr- and $PO_4^{'''}$- free monazite extract by this method.

Fe^{+++} interfere, but the following ions have no effect on the pptn.: Zn, Cd, Ca, Ba, Sr, Mg, Ni, Co, Pb^{++}, Mn^{++}, Cu, Be and Al. C. J. KEATTCH

1228. **Determination of nitrogen in zirconium by micro-Kjeldahl steam distillation.** J. F. Rodgers and G. J. Harter (*Anal. Chem.*, 1954, **26** [2], 395–396).—A method described for determining nitrogen in Zr comprises Beeghly's micro-Kjeldahl steam-distillation method modified by use of a 1-litre steam-generating flask and a Glass-Col spherical heating mantle, a HCl - HF mixture as the dissolving soln., and a Fisher electrophotometer (accommodating 50-ml Nessler tubes) for measuring the colour of the nesslerised distillate. A single determination can be made in half an hour or less, and 160 in 8-hr. The average deviation from the mean for $\simeq$ 50 determinations on a Zr sample containing 0·0034 per cent. of nitrogen was found to be $\pm$ 0·0007. Similar results on a standard sample of Zr containing 0·016 per cent. of nitrogen gave an average deviation of $\pm$ 0·001. Minute traces of nitric acid and ammonia fumes affect the accuracy of the results. Results of vacuum fusion were found to be consistently low compared with Kjeldahl distillation methods, probably because some of the nitrogen is held by the Zr in the molten state.

O. M. WHITTON

1229. **The removal of phosphate as zirconium phosphate in qualitative analysis.** D. J. Cole and D. W. Wilson (*Analyst*, 1954, **79**, 174–176).—The effectiveness of the removal of $PO_4^{'''}$ by Zr salts was investigated principally on the semi-micro scale, the effect of various factors being studied as well as the extent of co-pptn. of various cations. The following recommended procedure was developed. The acidity of the filtrate from the acid sulphide group is adjusted to less than *N* in HCl and $\simeq$ 0·2 g of solid NH_4Cl per ml is added. A 10 per cent. soln. of $ZrO(NO_3)_2.2H_2O$ in *N* HNO_3 is then added until pptn. is complete, more than a small excess of reagent being avoided. The mixture is heated to boiling and the ppt. is removed by centrifugation. The supernatant liquid and washings are then examined for metals in the other groups in the usual way. The excess of Zr accompanies Fe and does not interfere with the usual tests for it. A. O. JONES

1230. **The infra-red spectra of some inorganic phosphorus compounds.** D. E. C. Corbridge and E. J. Lowe (*J. Chem. Soc.*, 1954, 493–502).—Details are given of the i.r. spectra of 92 salts of phosphorus oxyacids, which were examined as fine powders in the 5000 to 650-cm^{-1} region. Characteristic frequencies are suggested for P—N and P—O—P linkages. Absorption frequencies are largely independent of the cation, except for Ag, but vary considerably with the anion. General absorption bands for each class of anion are listed and discussed. The effects of crystal and molecular structure are also considered and some structural information is derived. D. LIFF

1231. **Filter-paper chromatographic analyses of phosphate mixtures.** J. P. Crowther (*Nature*, 1954, **173**, 486).—The procedure described by Westman and Scott (*Nature*, 1951, **168**, 740) has been improved, so as to enable any mixture of ortho-, pyro, tri-, trimeta- or tetrametaphosphates to be separated into bands. The solvent consists of a mixture of *tert.*-butanol, water and formic acid (80:20:5). The blue molybdophosphate colour is developed by u.v. irradiation, and the amount of P in each band is determined colorimetrically with a standard deviation of $\pm$ 0·8. Components containing $>$ 4 atoms of P remain on the starting line. Components containing up to 9 P atoms may be separated by use of the solvent mixture *n*-propanol - H_2O - aq. NH_3, sp. gr. 0·88, (60:20:20), but the separation is not so clearly defined. H. P. PAGET

1232. **New method for precipitating ammonium magnesium phosphate. Determination of phosphate ion in phosphoric acid, alkali and alkaline-earth phosphates and natural calcium phosphates.** H. de Saint-Chamant and R. Vigier (*Bull. Soc. Chim. France*, 1954, **21** [2], 180–188).—$Mg\,NH_4PO_4.6H_2O$ is progressively and quant. pptd. from $\simeq$ 150 ml of orthophosphate soln. (prepared from 1 g of sample)

in presence of 60 ml of aq. NH_4Cl and $MgCl_2$ by the slow evolution of nascent NH_3 from the NH_4Cl and 20 ml of aq. 20 per cent. ethylamine (dissociation const. $= 3 \times 10^{-5}$). Sequestration of Ca, Fe^{III}, Al and Ti is effected by addition of $\simeq$ 50 ml of a neutral soln. containing 4 g of ethylenediaminetetra-acetic acid and 10 ml of aq. 50 per cent. lactic acid. The latter does not retard pptn. (as does citric acid), whilst its Ca salt is $\simeq$ 20 times as sol. as Ca tartrate. The large, euhedral crystals of the ppt. are easily decanted and washed. The full procedures for applying the method to (*i*) H_3PO_4, alkali phosphates, etc., or (*ii*) pptd. phosphates, natural Ca phosphates and superphosphates (including water-sol. and citric acid insol.) are described. The method is claimed to be rapid, accurate and precise to within $\pm$ 0·4 per cent.
W. J. BAKER

1233. **Spectrophotometric determination of sodium hypophosphite as a molybdenum-blue complex.** A. P. Scanzillo (*Anal. Chem.*, 1954, **26** [2], 411–412).—A spectrophotometric method for determining sodium hypophosphite is based on the blue colour produced by hypophosphorous acid or hypophosphites with ammonium molybdate and sulphurous acid. The method is applicable in the presence of sodium phosphite and of nickel chloride, but phosphates interfere. The method can be used in conjunction with the molybdovanadophosphoric acid method for determining H_3PO_3 and H_3PO_2 in mixtures. O. M. WHITTON

1234. **Rapid photometric determination of small quantities of alkali hexametaphosphate.** H. W. Thoenes and G. Kosfeld (*Z. anal. Chem.*, 1953, **140** [1], 9–14).—The red ferric thiocyanate complex is quant. decolorised in neutral soln. by alkali hexametaphosphate solutions. The relationship of this reaction with time, concentration, etc., is studied.

Procedure—To 100 ml of the test soln., add 1 ml of standard Fe^{III} solution [0·7022 g of $(NH_4)_2SO_4.FeSO_4.6H_2O$ in 50 ml of 15 per cent. H_2SO_4 soln., oxidised to Fe^{III} with $KMnO_4$ and made up to 1 litre], 1 ml of HCl (1 + 1) and 5 ml of KCNS soln. (20 per cent. w/v). Measure the absorption through a green filter and read the hexametaphosphate concn. from a calibration graph. As little as 0·05 mg per litre can be estimated. Pyrophosphates interfere, but orthophosphates only when present at higher concentrations. The determination takes 1 to 2 min. P. S. STROSS

1235. **Polarographic determinations of antimony in lead - antimony alloys.** H. F. Hourigan and J. W. Robinson (*Anal. Chim. Acta*, 1954, **10** [3], 281–291).—It is known that the reduction of Sb gives rise to two polarographic steps, one at $E_{\frac{1}{2}} \simeq 0$ V and the other at $-$ 0·15 V. In the presence of Pb these steps merge and give rise to errors. An attempt was made to define the limits of concn. of Pb and acid that could be present without affecting the accuracy of the determination. Polarograms were taken with Pb soln. at concn. up to 0·03 *M* and HCl at concn. between 2 and 9 *M*. Changes in the diffusion current due to the Sb at a series of points in that range were plotted to give contours of step height. Pb affects the Sb in two ways (*i*) as a constituent of the base soln. as described by Vivarelli (*Anal. Chim. Acta*, 1952, **6**, 379) Pb alters the $E_{\frac{1}{2}}$ of the two steps unequally and brings them close together, and (*ii*) by the formation of $PbSbCl_7$. The $E_{\frac{1}{2}}$ of $Sb^{\cdots\cdots}$ to $Sb^{\cdots}$ is clearly altered by this complex formation. The addition of alkali chlorides decreases the Pb ion concn. Although LiCl, aq. NH_3 and KCl were all satisfactory, KCl was finally decided upon. The method gave good results within the ranges 4 to 8 *M* for HCl, 0 to 0·03 *M* for Pb and 0 to 0·002 *M* for Sb. Within these limits Sb concn. is proportional to the step height, with $E_{\frac{1}{2}} \simeq -$ 0·15 V, *i.e.*, the $Sb^{\cdots}$ - Sb amalgam step is independent of the initial state of the Sb. The concn. of HCl must be the same for the standard and the sample, as the Sb wave varies with the base soln. Full experimental details are given. B. LAMB

1236. **Electrolytic deposition of tin from solutions of its chloride.** A. Foschini (*Z. anal. Chem.*, 1953, **139** [6], 408–412).—The deposition of Sn from acid solutions of its chloride is studied. The limiting concn. of HCl when the platinum electrodes are coppered or when they are not, and in presence or absence of ammonium oxalate is found. It is unnecessary to copper the electrodes or to add ammonium oxalate to attain quant. separation.

The maximum HCl concn. suitable under those conditions is 12·5 per cent. at a current of 1 amp. It is unnecessary to separate iron. As Sn^{II} deposits more easily than Sn^{IV}, oxidation of the soln. before electrolysis is not necessary. P. S. STROSS

1237. **Use of thiourea dioxide in micro-analysis. Micro-determination of tin.** C. van Nieuwenburg and J. W. L. van Ligten (*Chim. Anal.*, 1954, **36** [2], 41–42).—Thiourea dioxide (formamidinesulphinic acid) is prepared by treating aq. thiourea with H_2O_2. The heavy metals Cd, Pb, Sn, Ni, Co, As, Sb, Cu, Ag, Hg and Bi are pptd. from NH_3 soln. or suspension by thiourea dioxide as mixtures of metals and sulphides. Precipitation of Sn, As, Cu, Hg and Sb, is complete and a method for the micro-determination of Sn as SnS is described. Thioacetamide is added to ensure complete pptn. The ppt. is washed with acetic acid. C. G. TAYLOR

1238. **Radioactive method for the determination of tantalum in ferroniobium and niobium ores.** A. Kohn (*Chim. et Ind.*, 1954, **71** [1], 69–77).—The sample to be analysed and standards, consisting of Fe powder mixed with known amounts of Ta, are irradiated in an atomic pile and set aside for $\simeq$ 7 days to reduce the activity of short-life radio-isotopes resulting from impurities. The γ-activity is then measured and the Ta content of the sample is determined after allowance has been made for the slight activity of the Fe powder. Possible sources of error are discussed. The relative error in relation to the average values obtained is considered to be $< \pm$ 5 per cent. J. M. JACOBS

1239. **Use of ultra-violet rays in analytical chemistry. IV. Colorimetric determination of bismuth in presence of large amounts of lead.** I. A. Stolyarova (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 270–278).—Bi (25 to 100 μg) is determined in presence of large amounts of Pb (20 mg) from measurements of the absorption at 365 mμ of the KBr complexes on the photometer described previously (*Brit. Abstr. C*, 1953, 407). Fairly large amounts of Fe (20 mg), Zn and Cd (50 mg), Hg, Sn and As (10 mg), Sb (20 mg), and Cu (2 mg or, after reduction with ascorbic acid, 15 mg) do not interfere. The method is suitable for determining 0·01 per cent. of Bi in metallic Pb. The sensitivity is 0·2 μg of Bi in 1 ml. G. S. SMITH

1240. **Direct bromimetric titration of the oxinates of bismuth, iron, copper and other metals.** A. I. Busev (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 299–301).—An electrometric method is described. G. S. SMITH

1241. **Optical method for measurement of small amounts of oxygen in a helium atmosphere.** J. W. Moyer and W. A. Ruggles (*J. Opt. Soc. Amer.*, 1954, **44** [1], 86–87).—A physical method is described for measuring O concn. from < 1 p.p.m. to several p.p.m. in the presence of an inert-gas atmosphere. The gas to be analysed circulates over a sodium surface, prepared by a special method which produces a flat mirror-like surface of orientated crystals. The thickness of the resulting oxide film is determined by using a Babinet compensator to measure the phase difference produced in a beam of monochromatic light reflected from the surface. The presence of a small amount of nitrogen appears to be necessary in order for the oxidation reaction to proceed with reasonable rapidity. B. S. COOPER

1242. **The determination of low concentrations of oxygen in gases by the manganous hydroxide method.** H. A. C. van Straten (*Anal. Chim. Acta*, 1954, **10** [3], 243–255).—A.S.T.M. method D1021–49T, which is a version of the Winkler method, gives high results for O concn. < 0·5 per cent. and low results for O concn. > 0·5 per cent., these findings being based on mass-spectrometric determinations. The following modifications of an earlier method (*Brit. Abstr. B*, 1935, 724) ensure a reproducibility of 3·6 per cent. of the O content in the range 0·1 to 4 per cent. of O and of 0·004 per cent. of the total vol. for O concn. of < 0·1 per cent. First, the reaction vessel and reagents are de-aerated by heating to 50° C *in vacuo*. Secondly the $MnCl_2$ concn. is reduced from 5 to 2 ml of saturated soln. in 100 ml of water so as to produce a finely divided ppt. of $Mn(OH)_2$. This condition produces more foaming and better contact with the gas. Thirdly the $Mn(OH)_2$ suspension is shaken continuously with the gas for 1 hr. No interference arises from the presence of unsaturated hydrocarbons, including acetylene, or carbon monoxide. W. C. JOHNSON

1243. **The absorptiometric determination of dissolved oxygen.** J. Banks (*Analyst*, 1954, **79**, 170–173).—The use of 3:3′-dimethylnaphthidine as a colorimetric reagent for dissolved O in boiler feed water (0 to 0·1 ml per litre) is described. The O is first converted to its I equiv. by the Winkler reaction with $MnCl_2$, alkaline KI and finally dil. H_2SO_4. An aliquot is buffered with a Na acetate - acetic acid buffer and a soln. of 3:3′-dimethylnaphthidine in glacial acetic acid is added. The colour intensity is measured absorptiometrically within 15 min., and the dissolved O concn. is ascertained from a calibration graph prepared with 0·001 *N* I soln. A. O. JONES

1244. **Determination of oxygen in sodium.** J. C. White, W. J. Ross and R. Rowan, jun. (*Anal. Chem.*, 1954, **26** [1], 210–213).—A 1 to 20-g sample of Na metal containing 0·001 to 0·1 per cent. of oxygen is extracted with 100 ml or more of *n*-butyl bromide and *n*-hexane (1 + 1) for 1 to 2 hr. at 60° to 70° C. After cooling and diluting with 100 to 200 ml of CO_2-free water, the aqueous phase, containing NaOH derived from the Na_2O only, is separated and titrated potentiometrically (glass electrode) with 0·001 *N* HNO_3. NaOH and Na_2CO_3 present in the Na interfere; the standard deviation over a range of oxygen concentrations is ± 0·003 to 0·005 per cent. D. A. PANTONY

1245. **Critical factors in determination of oxygen in titanium by the vacuum-fusion method.** W. M. Albrecht and M. W. Mallett (*Anal. Chem.*, 1954, **26** [2], 401–402).—A systematic study is reported of the operating details of the various methods for determining oxygen in titanium by the vacuum fusion method. With the apparatus used, gas volumes can be determined with a sensitivity equivalent to 0·001 per cent. w/w of oxygen in a 0·5-g sample. The average blank correction for the apparatus is 0·001 per cent. w/w. Results are reported and the advantages of using small samples weighing 0·5 g or less with a tin flux and a crucible cover are discussed. Analyses for double arc-melted iodide titanium with no TiO_2 addition give the base O levels for the arc-melted standards and a measure of the original O content of the metal plus that picked up during arc melting. The estimated total O of each standard is the summation of this base value and the weighed addition of O as TiO_2. Results in the present work for a multiplicate series of vacuum fusion analyses have a range somewhat less than the ± 10 per cent. generally attained. The experimental values also agree with the estimated oxygen content within ± 10 per cent. with an over-all average of about ± 6 per cent. O. M. WHITTON

1246. **A method to determine simultaneously small quantities of hydrogen sulphide and carbon disulphide in air.** W. Sonnenschein and K. Schäfer (*Z. anal. Chem.*, 1953, **140** [1], 15–25).—By the simple, rapid and sensitive method described, it is possible, by use of special gas absorption apparatus (illustrated), to determine minute quantities of H_2S and CS_2 in the air. H_2S is determined by the colorimetric estimation (at 670 mμ) of the methylene blue formed when H_2S reacts with a 0·1 per cent. soln. of dimethyl-*p*-phenylenediamine hydrochloride in 18 per cent. HCl and 0·5 per cent. $FeCl_3.6H_2O$ in 4 per cent. HCl. CS_2 reacts with sodium diethyldithiocarbamate and copper acetate to give the yellow cupric diethyldithiocarbamate (extinction measured at 430 mμ). As little as 0·2 μg of H_2S and 0·6 μg of CS_2 can be measured with an accuracy of ± 20 per cent. Colloidal ZnS is a stable standard for the H_2S calibration graph. The complete determination takes 1½ hr. P. S. STROSS

1247. **The volumetric determination of sulphates.** J. R. Gwilt (*Chem. & Ind.*, 1954, [11], 309).—The method of Munger *et al.* (*Brit. Abstr. C*, 1951, 127) can be simplified to give a rapid routine assay of sulphate in certain pharmaceuticals. Precision is ≃ 0·1 mg for 20 to 50 mg of Na_2SO_4. B. J. W.

1248. **Microchemical determination of sulphate by the chromate method.** W. Geilmann and G. Bretschneider (*Z. anal. Chem.*, 1953, **139** [6], 412–423).—Neutralise 15 ml of a solution containing up to 1·2 mg of SO_4'' to *p*-nitrophenol (1 drop of 0·2 per cent. soln.) and acidify with 1 drop 0·1 *N* HCl. Add 2 drops of a suspension of $BaSO_4$ and add slowly 2 ml of 0·008 *M* $BaCl_2$. Set aside for 1 hr. and precipitate excess of Ba with 2 ml of 0·01 *M* $K_2Cr_2O_7$, heat on water-bath, add 0·25 ml of 10 per cent. Na acetate, shake and allow to cool. After 1 hr. make up to 25 ml, mix and centrifuge. To 20 ml of the supernatant liquid add 8 ml of 50 per cent. H_2SO_4 and *o*-phenanthroline - ferrous sulphate

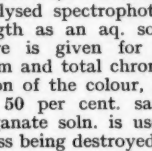
(ferroin). Titrate with ferrous sulphate to the maximum red colour. Carry out a blank determination in similar manner. Ca, Al and Fe^{III}, in particular, interfere with $BaSO_4$ pptn. and give low results. The general use of this micro-method is not recommended. P. S. STROSS

1249. **Chromium: toxic behaviour and colorimetric determination.** J. E. Delaney (*Sanitalk*, 1953, **1** [2], 9–13).—The toxicity of sexavalent chromium and its effect on sewage treatment are briefly discussed and a method for its spectrophotometric determination is described. In the standard method *s*-diphenylcarbazide is added to the aq. soln. of sexavalent chromium to form a coloured compound. From investigations it was found that this compound can be quantitatively extracted with, and concentrated in, *iso*pentanol and analysed spectrophotometrically at the same wavelength as an aq. soln., *viz.*, 543 mμ. The procedure is given for determining sexavalent chromium and total chromium. To accelerate the extraction of the colour, salt solution is added to form a 50 per cent. saturated aq. soln. Acid permanganate soln. is used to oxidise chromium, the excess being destroyed by sodium azide.

WATER POLLUTION ABSTR.

1250. **The reaction of chromate with diphenylcarbazide. I and II.** M. Bose (*Anal. Chim. Acta*, 1954, **10** [3], 201–208; 209–221).—I. The red-violet colour produced by the reaction of CrO_4'' and diphenylcarbazide (**I**) is produced also by CrO_4'' and diphenylcarbazone (**II**) and by $Cr^{··}$ and **II**. Absorption spectra indicate that the coloured product is the same in each reaction. An excess of CrO_4'' or of $Cr^{··}$ in the respective reactions destroys the colour. No colour is given by $Cr^{··}$ and **I** nor by $Cr^{···}$ with **I** or **II**. It is concluded that the colour produced in each reaction is due to a compound of $Cr^{··}$ with **II**, and the absorption spectra of mixtures of CrO_4'' and **I** in various proportions indicate that only one coloured substance is formed. This substance does not undergo electrolytic migration and it has, to a degree, the solubility characteristics of a non-polar compound. It is therefore assumed to be an "inner complex."

II. The three reactions in which the colour is produced are further examined by Job's methods (*Brit. Abstr. A*, 1928, 589). By use of various proportions of equimolecular solutions of the reactants, the proportions corresponding with maximum colour development are determined. The results suggest that the complex is formed by replacement of two H atoms in **II** by $Cr^{··}$ and that the reactions are as follows: (*i*) $2Cr^{·····} + 3\mathbf{I} \rightleftarrows 2$ [complex] $+ C_6H_5N{:}N{\cdot}CO{\cdot}N{:}NC_6H_5$ (**III**) $+ 4H^{·}$, (*ii*) $Cr^{·····} + 3\mathbf{II} \rightleftarrows$ [complex] $+ 2\mathbf{III} + 2H^{·}$ and (*iii*) $Cr^{··} + \mathbf{II} \rightleftarrows$ [complex] $+ 2H^{·}$. The respective equilibrium constants for each reaction determined under various conditions and calculated on the bases of the above equations, are consistent enough to support the postulated mechanisms. Magneto-chemical experiments confirm the presence of $Cr^{··}$ in the complex, whose formula is stated to be—



W. C. JOHNSON

1251. **Extraction of molybdenum with ether from hydrochloric acid solutions.** I. P. Alimarin and V. N. Polyansky (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 266–269).—Small amounts of Mo, *e.g.*, 2 mg in 50 ml of soln., can be extracted rapidly and quantitatively with ether at a HCl concn. of 5 to 6 *N*. An automatic extraction apparatus is described. G. S. SMITH

1252. **Reduction by aluminium powder in aqueous-solution titrimetric determination of molybdenum.** E. R. Riegel and R. D. Schwartz (*Anal. Chem.*, 1954, **26** [2], 410–411).—In a method for the titrimetric determination of Mo in aqueous soln., a fine Al powder (Reynolds No. 400) is used as reducing agent, and N gas is used both to prevent oxidation of Mo^{III} by air and to provide the necessary stirring. The method has certain advantages over the silver and the Jones reductor procedures, but gives similar results.

O. M. WHITTON

1253. **The semiquantitative determination of tungsten in niobium - tantalum products and the separation of tungsten from niobium and tantalum. Contributions to the chemistry of niobium and tantalum. XI.** H. Schäfer with C. Pietruck and U. Grözinger (*Z. anal. Chem.*, 1954, **141** [1], 24–33).—The oxide mixture is heated with CCl_4 in a closed tube. Red $WOCl_4$ is formed at 250° C and reacts with more CCl_4 to give WCl_6 at 330° to 350° C. $NbCl_5$ and $TaCl_5$ are formed by this treatment. WCl_6 can be separated by treatment with CCl_4, in which $NbCl_5$ and $TaCl_5$ are insoluble. W is estimated by comparison of the violet soln. with colour standards. Ti, Zn and Fe do not interfere. The separation of Nb and Ta is best achieved by pptn. of sodium niobate and tantalate in the presence of NaCl.

C. G. TAYLOR

1254. **Potentiometric titration of milligram quantities of uranium in the presence of iron.** R. B. Hahn and M. T. Kelley (*Anal. Chim. Acta*, 1954, **10** [2], 178–181).—Uranium in mg quantities can be determined by semi-micro titration of $U^{····}$ with $Ce(SO_4)_2$, $K_2Cr_2O_7$ or $KMnO_4$. The reduction of $U^{·····}$ with a slight excess of chromous sulphate, followed by potentiometric titration of the $U^{····}$ with standard $Ce(SO_4)_2$ in an atmosphere of CO_2 has been successfully used at the Oak Ridge National Laboratory. This method cannot be used in the presence of Fe at room temp., as $Fe^{···}$ is reduced to $Fe^{··}$, which is then titrated along with the $U^{····}$ causing error. At temp. above 60° C the Fe does not interfere, but the practical difficulties of working with small quantities at elevated temp. makes this method of little use. This interference can be overcome by complexing $Fe^{··}$ with 1:10-phenanthroline. The oxidation potential of the $Fe^{··}$ - $Fe^{···}$ system is changed and the Fe no longer interferes with the titration. A precision and accuracy of about 1 per cent. is claimed for samples containing only U and Fe as metallic constituents. Other non-reducible cations (Al, Ni, etc.), do not interfere, but their presence may cause some decrease in accuracy. B. LAMB

1255. **New method for the determination of chlorine in the presence of bromine.** L. Nebbia and B. Pagani (*Chim. e Ind.*, 1954, **36** [1], 14–16).—Br liberated by addition of $KBrO_3$ to a soln. containing Cl', Br' and H_2SO_4 at 15° to 20° C reacts with amylene or di*iso*butylene in CCl_4; the Cl' remaining in the aq. layer is determined argentimetrically. R. C. MURRAY

1256. **Determination of iodide.** K. G. Stone (*Anal. Chem.*, 1954, **26** [2], 396–397).—In a method given for determining I in the presence of chloride, or of chloride and bromide with iodate as the oxidising agent and substitution of the dead-stop end-point for a slower potentiometric end-point, $CHCl_3$ is used as solvent in the titration media to prevent precipitation of iodine and thus to eliminate co-precipitation of potassium tri-iodide. The results for iodide in the presence of chloride are satisfactory, and those in the presence of bromide rather less so. O. M. WHITTON

1257. **Alkalimetric determination of iodine.** B. Stempel (*Z. anal. Chem.*, 1954, **141** [2], 100–101).—An excess of hydrazine sulphate soln. (approx. 0·5 per cent. neutralised to methyl red with 0·1 *N* NaOH) is added to the iodine soln. of unknown strength. After 15 min. the liberated acid is titrated with 0·1 *N* NaOH. One litre of *N* NaOH ≡ 0·8 × 126·92 g of I. C. J. KEATTCH

1258. **Argentimetric [micro-determination and macro-] determination of iodine.** B. Stempel (*Z. anal. Chem.*, 1954, **141** [2], 101–102).—Excess of hydrazine sulphate soln. (neutralised to methyl red with NaOH) is added to the unknown soln. of I. After 15 min., the liberated HI is titrated with standard $AgNO_3$ soln., 1 to 5 drops of 0·5 per cent. eosin are used as indicator and the titration is continued until the soln. suddenly turns crimson. C. J. KEATTCH

1259. **A critical examination of the use of activated charcoal for the analytical separation of elementary iodine from ionised iodine.** H. Spitzy, H. Skrube and F. S. Sadek (*Z. anal. Chem.*, 1953, **140** [2], 110–121). Earlier work (Stempel, *Brit. Abstr. C*, 1952, 96) on the separation of iodine from iodide and iodide from other halide ions by means of charcoal is repeated. The adsorption capacity for I of various types of charcoal, treated or untreated, is studied in relation to time and pH, and their suitability is discussed. It is found that adsorbed I is partly reduced to iodide. Adsorbed I is best removed from charcoal by KOH soln.; direct titration of the charcoal, on which I is adsorbed, with thiosulphate gives errors owing to adsorption of thiosulphate. None of the methods studied is suitable for a precise determination. P. S. STROSS

1260. **Differential thermal analysis of synthetic manganese dioxide.** N. S. Krishna Prasad and C. C. Patel (*J. Indian Inst. Sci., A*, 1954, **36** [1], 23–31).—Differential thermal analysis of various samples of MnO_2 was carried out from room temp. to 1100° C by means of Pt - Pt(Rh) thermocouples. Corrosion of the thermo-element occurred during heating with synthetic MnO_2, and with each sample a correction curve had to be drawn; Al_2O_3 was used in each sample-holder. Corrosion may explain the divergent results obtained by previous workers. Endothermic peaks at 620° and 990° C are attained with pyrolusite, and peaks at 560° to 580° C and 950° to 970° C are attained with different samples of γ-MnO_2; initial slow exothermic changes that occurred with some samples are attributed to sintering. A sample obtained by oxidation of $MnSO_4$ soln. with $KMnO_4$ gave endothermic peaks at 120°, 520° and 940° C, so resembling cryptomelane. Comparison of these results with those obtained from four commercial samples of MnO_2 enabled qual. identification to be made of the crystallographic species present. H. P. PAGET

1261. **The polarographic determination of manganese, copper, chromium and iron in the insoluble residue remaining after the solution of calcium metal in hydrochloric acid.** G. F. Reynolds and H. I. Shalgosky (*Anal. Chim. Acta*, 1954, **10** [3], 273–280).—The insoluble residue left after treating Ca metal with HCl is ignited and dissolved of 2 ml of 12 *M* $HClO_4$ by heating gently in a boiling-tube fitted with a "cold finger" condenser. The soln. is transferred to a 25-ml flask, a mixture of 5 ml of 15 per cent. mannitol soln. and 5 ml of 10 *M* NaOH is added as base electrolyte and the soln. is made up to 25 ml. The soln. is deoxygenated and the polarogram is recorded over the range − 0·4 to − 1·7 V using H_2SO_4 - Hg_2SO_4 - Hg as anode. The heights of the steps due to Mn, Cu, Cr and Fe, which occur at $E_{\frac{1}{2}}$ − 0·78, − 1·0, − 1·2 and − 1·5 V, respectively, are measured. The Cu and Mn steps are very close together and a method of measurement to overcome this effect is given. B. LAMB

1262. **Analytical aspects of reactions of 2-(2-pyridyl)benziminazole and 2-(2-pyridyl)iminazoline with [ferrous] iron.** J. L. Walter and H. Freiser (*Anal. Chem.*, 1954, **26** [1], 217–221).—2-(2-Pyridyl)-benziminazole and 2-(2-pyridyl)iminazoline give, respectively, an intense red or purple-red colour with Fe^{++}, but Cu^{+}, Hg^{++} and Co^{++} give precipitates or different colours. The light absorption curves for the Fe^{++} complexes are given, and the effect of pH, reagent concn. and extraneous ions, and stability of the colours are discussed in connection with the determination of Fe with these reagents The benziminazole is sensitive to 2 μg of Fe^{++} per ml, and the sensitivity is increased by extraction of the complex with *iso*pentanol. D. A. PANTONY

1263. **Coulometric titration of thiosulphate with iodine. Application to the determination of oxidising agents.** K. Rowley and E. H. Swift (*Anal. Chem.*, 1954, **26** [2], 373–375).—By the investigation reported, the feasibility of the coulometric titration of thiosulphate with iodine was determined, and the limiting conditions were established. Results presented show that Fe^{+++} is titrated satisfactorily only if O is carefully removed from all solutions, and that errors in the dichromate titrations are within those of the experimental measurements. O. M. WHITTON

1264. **Spectrophotometric determination of iron in vanadium, chromium, manganese, nickel and zinc. 1:10-Phenanthroline rate phenomena.** D. W. Margerum and C. V. Banks (*Anal. Chem.*, 1954, **26** [1], 200–202).—As VO^{++}, Cr^{+++}, Ni^{++}, Mn^{++} and Zn^{++} (as ammine complex) react more slowly with 1:10-phenanthroline than Fe^{++}, solvent extraction or spectrophotometric separation is possible. A 0·25 to 0·5-g sample of V, Cr, Mn, Ni or Zn is dissolved in acids, and the oxidation state is adjusted with $NH_2OH.HCl$. After control of pH (4 to 5 for V, 2 to 3 for Cr and Ni), 1 ml of *M* $NaClO_4$ and 20 ml of 0·1 per cent. 1:10-phenanthroline are added and the ferroin perchlorate is extracted with 2 successive 20-ml portions of nitrobenzene. After drying the extract with Na_2SO_4, the absorbancy is measured at 515 mμ. Mn is treated similarly, except that the ferroin perchlorate is determined directly on the aq. soln. at pH 2 to 3 and 510 mμ. Zn is converted to the ammine complex with NH_4Cl and aq. NH_3 and the ferroin absorbancy is

measured at 510 mμ. Less than 0·4 per cent. of Cu and Co do not interfere at pH < 5. Errors are claimed to be generally < ± 0·5 per cent.
D. A. PANTONY

1265. **Direct photometric determination of iron, titanium and copper in tantalum and its oxide.** J. Hastings, T. A. McClarity and E. J. Broderick (*Anal. Chem.*, 1954, **26** [2], 379–381).—Rapid chemical methods described for analysing Ta metal are based on the formation of soluble complexes of Ta with tartrates and oxalates, the soln. being stable enough to provide media for colorimetric reactions that are specific for the elements to be determined. Data for preparing calibration curves for spectrographic examination of the material are given. The spectrophotometric determination of Fe by *o*-phenanthroline is found to be reproducible in the range of 0·002 to 0·030 per cent. of Fe, of Cu by sodium diethyldithiocarbamate in the range of 0 to 0·016 per cent. of Cu, and of Ti by H_2O_2 and H_2SO_4 in the range of 0·004 to 0·070 per cent. Ti. Calibration data for each element are obtained with a Beckman DU spectrophotometer. Tedious separations of the elements to be determined are unnecessary and contamination from large quantities of reagents is avoided. The time gained in analysing Ta metal samples is ten-fold and precision and accuracy are greatly improved.
O. M. WHITTON

1266. **Separation of inorganic cations by precipitation through diffusion in gels. I.** M. Milone and G. Cetini (*Ann. Chim., Roma*, 1953, **43** [10], 648–651).—Diffusion of a solution containing Fe^{III} and Cu^{II}, etc., into precipitants (Na_2SiO_3, Na_2HPO_4, etc.) yields banded precipitates in which each band corresponds to a precipitate of one of the diffusing ions.
R. C. MURRAY

1267. **Suggested method of evaluating the porosity of coatings on ferrous metals.** T. W. Farrer (*Chem. & Ind.*, 1954, [3], 77–78).—The method is based on the rapid rate of attack on Fe by aq. suspensions of elemental S. Specimens coated with Sn (hot-dipped or electro-deposited) or with an electro-deposited alloy of Zn (6 per cent.) and Fe (94 per cent.) are electrolytically degreased in 1 per cent. Na_2CO_3 at room temp. and then immersed in an aq. suspension of washed pptd. S (15 per cent. with or without 5 per cent. of bentonite). There is an induction period of several hr., during which the oxide film is replaced by sulphide. The induction period can be reduced by addition of a soluble sulphide to the suspension. Thereafter the rate of attack is rapid and the presence of pores is readily demonstrated.
J. M. JACOBS

1268. **EDTA in metallurgical analysis, especially for the determination of nickel and zinc.** H. Flaschka (*Chemist Analyst*, 1953, **42** [4], 84–86).—The use of ethylenediaminetetra-acetic acid (**I**) in the determination of metals is reviewed. Methods are described for the determination of Ni and Zn. Ni is pptd. with dimethylglyoxime and the ppt. is removed and dissolved in dil. HCl. The acidic soln. is treated with an excess of 0·1 *M* **I** soln. and neutralised with aq. NH_3, and a buffer soln. is added containing 13·4 g of NH_4Cl and 88 ml of conc. aq. NH_3 in 250 ml of soln. Eriochrome black T indicator powder (1 pt. Eriochrome black T with 400 pt. NaCl) is added and the excess of **I** is titrated with a standard Zn soln. Alternatively the acid soln. of Ni - dimethylgloxime complex is treated with K Mg ethylenediaminetetra-acetate and after buffering, the liberated Mg is titrated with standard **I**. Zn is pptd. as $ZnHg(CNS)_4$ and the ppt. is dissolved in HCl and 10 per cent. aq. KI. The soln. is neutralised, buffer soln. is added and the soln. is titrated with **I** and Eriochrome black T indicator. Alternatively the $ZnHg(CHS)_4$ is dissolved in 10 per cent. aq. KCN, diluted to 50 to 100 ml. treated with 5 ml of aq. formaldehyde (40 per cent. soln.) or chloral hydrate (20 per cent. soln.), buffered and titrated with **I**. In a third method the $ZnHg(CNS)_4$ is slurried with water and an excess of **I** is added. After buffering, the excess is determined with 0·1 *M* Zn soln. Results are satisfactory for both Ni and Zn.
D. BAILEY

1269. **Spectrophotometric determination of nickel by heptoxime.** J. Gillis, J. Hoste and Y. van Moffaert (*Chim. Anal.*, 1954, **36** [2], 43–47).—The Ni - *cyclo*heptanedionedioxime (heptoxime) complex is pptd. from acid soln. and is sol. in $CHCl_3$ to give a yellow soln. that obeys Beer's law over the range 1 to 10 μg of Ni per ml. The wavelength for max. absorption is 377 mμ and the mol. extinction coeff. is 4660. The Ni - heptoxime complex has a solubility in $CHCl_3$ of 47·2 mg per 100 ml compared with 5 mg per 100 ml for Ni - dimethylglyoxime. The colour is stable for at least 4 hr. and a 1000-fold excess of reagent does not interfere. The extraction of Ni is quant. over a pH range of 3·8 to 11·7. The interfering effects of Al^{+++}, Ba^{++}, Ca^{++}, Cd^{++}, Cr^{+++}, Mg^{++}, Mn^{++}, NH_4^+, Na^+, K^+, Sr^{++}, Zn^{++}, Mo^{+++++}, V^{+++++}, W^{++++++}, Cl', Br', NO_3', ClO_4', SO_4'', HPO_4'', tartrate, borate and phthalate in 100-fold excess are insignificant. Co^{++}, Cu^{++} and Fe^{++} interfere by forming $CHCl_3$-soluble heptoxime complexes that absorb u.v. light. These interferences are eliminated by the addition of thiosulphate (Fe^{++} must first be oxidised to Fe^{+++}). Under these conditions Ni can be determined in the presence of 1000, 100 and 50 times the quantities of Fe^{+++}, Cu^{++} and Co^{++}, respectively.
C. G. TAYLOR

1270. **Spectroscopic estimations on natural minerals.** G. A. Monnot (*Spectrochim. Acta*, 1954, **6** [2], 153–157).—A. *Silica in fluorspars.* Samples containing 0·05 to 5 per cent. of SiO_2 are estimated spectrographically with a precision of 10 per cent., the intensity of the lines Si I 2516·1 and Si I 2519·2 being compared with that of Ca I 2721·6. The limit of sensitivity for a 20-mg sample is 10 μg of silica.

B. *Fluorides in siliceous rocks.* It is shown that silica inhibits the appearance of the CaF_2 bands in the spectrographic analysis of CaF_2 - SiO_2 mixtures, and amounts of CaF_2 less than 5 per cent. cannot be detected. A method is described in which the sample is mixed with 4 pt. of $CaCO_3$; 10 μg of F can be detected in a 4-mg sample. For samples containing 0·25 to 5 per cent. of F the precision is ± 10 per cent.
E. HAYES

1271. **Note on the analysis of ashes. Determination of trace elements in coal ash and in siliceous rocks.** G. A. Monnot (*Chim. Anal.*, 1953, **35** [11], 274–276).—Spark spectrography is used to determine Ge in ashes from oil and coal, Ni being added as an internal standard. Amounts of Ge corresponding to 5 to 300 g of GeO_2 per ton of ash can be determined. Samples of 20 metal oxides at known concentrations of 1, 0·1 and 0·01 per cent. in a ground-silica base of < 10-μ particle size have been prepared for use as spectroscopic standards for mineral analysis.
W. C. WAKE

1272. **The polarising microscope in the X-ray analysis of minerals.** E. G. Steward (*Analyst*, 1954, **79**, 173–174).—The polarising microscope provides a valuable supplement to X-ray techniques in the identification of constituents of mineral mixtures. In the first of two general types of problem, confirmation is required of the presence of a particular mineral (*e.g.*, pyrochlore) in a concentrate in an amount too low for detection in an X-ray powder photograph. Under the polarising microscope and when the main minerals have been identified by X-ray examination, a probable crystal of pyrochlore can be quickly and easily distinguished by qualitative observation of its optical properties. The fragment is then mounted and the normal type of rotating crystal X-ray photograph is obtained which is then superimposed on a powder photograph of known pyrochlore and the fragment is thus identified. In the second type of problem the principal minerals in a very complex mixture have to be distinguished and identified. The diffraction pattern may be too complex to permit use of the accepted index of X-ray data. Under the polarising microscope particular suspected constituents can be picked out and their identity confirmed by X-ray photography and comparison either with standard photographs or with reference data. A. O. Jones

1273. **The spectrochemical analysis of slags.** F. Baldi (*Spectrochim. Acta*, 1953, **6** [1], 39–52).—In preliminary experiments with samples merely powdered or powdered and formed into briquettes with conducting materials such as graphite, Cu, Bi or brass, exposures were made with an a.c. arc and controlled and uncontrolled sparks. Zn and Bi both give a high dispersion of results. In the main investigation the samples were powdered, mixed with Cu powder (1 + 1) and made into briquettes at a pressure of 20 kg per sq. mm. A controlled spark was used and the spectrum was photographed with a Zeiss "Qu 24" spectrograph with a 10-sec. exposure. Thirteen slags of known composition with respect to CaO (25 to 70 per cent.), SiO_2 (3 to 30 per cent.), MnO (2 to 25 per cent.), and FeO (5 to 20 per cent.) were investigated and standard curves are given for intensity comparisons at different suitable wavelengths by means of the mutual-standard method, which is critically examined. The reproducibility is investigated for the mutual-standard method and for Cu and Zn as internal standards; the first has better reproducibility. E. J. H. Birch

1274. **Spectrographic analysis of complex oxides with particular reference to slags and ores.** W. J. Price (*Spectrochim. Acta*, 1953, **6** [1], 26–38).—The material to be analysed is fused with borax and cobalt oxide as an internal standard, the cooled mixture is powdered, made into pellets with twice its weight of graphite powder and its arc spectrum between 245 and 350 mμ is photographed; a controlled d.c. arc is used with the sample as the positive electrode. Calibration curves are given for Fe, Ca and Si; the appropriate Co line for comparison for various percentage compositions is indicated in a table. The estimated time of working is 105 min. for 5, and 81 min. for 3 replicates. Detailed comparison of analyses of ores and slags by spectrographic and chemical methods are made, and there is a short statistical discussion. E. J. H. Birch

1275. **An evaporation method for measuring the resistivity-water saturation characteristics of cores.** J. Birks (*J. Inst. Petrol.*, 1954, **40**, 14–17).—A saturated calcium sulphate soln. of constant specific resistance is used in an evaporation method for measuring the resistivity-water saturation characteristics of bore-hole cores. Results are presented for typical sandstone and limestone samples. This evaporating liquid has constant composition and good electrical conductivity and volatility, and also does not form supersaturated solutions easily; it is present in most formation waters and since many limestone rocks contain anhydrite, solution of the latter is thus avoided. The method is applicable to cores having a complete range of permeability and porosity; it is rapid and reproducible, while permitting simultaneous measurements on a large number of cores. D. R. Glasson

See also Abstracts 1177, 1180, 1191, 1192, 1315, 1335, 1336, 1337, 1384, 1386, 1387.

3.—ORGANIC ANALYSIS

1276. **Hydrogen determination and liquid analysis with a beta-particle absorption apparatus.** V. N. Smith and J. W. Otvos (*Anal. Chem.*, 1954, **26** [2], 359–366).—Absorption of β-radiation by liquids depends on their composition and density. If the density of org. liquids is measured independently, H content can be estimated to within 0·1 per cent. The apparatus described can be used for continuous recording of density or composition of flowing liquid streams. J. Davis

1277. **Improved micro-Dumas method and apparatus.** T. D. Parks, E. L. Bastin, E. J. Agazzi and F. R. Brooks (*Anal. Chem.*, 1954, **26** [1], 229–232).—Modifications of the original micro-Dumas method and apparatus overcome (*i*) errors caused by incomplete oxidation of the methane, which forms during sample pyrolysis, and (*ii*) errors caused by incomplete combustion of carbonaceous residues, which may contain N. The first are eliminated by an auxiliary combustion tube filled with highly active CuO; the sample is pyrolysed in a stream of CO_2 by a travelling electric furnace, the carbonaceous residue then being completely burned in O. Other modifications include substitution of the Cu-CuO filling with Ni-NiO and the use of a mercury-filled wt. azotometer instead of one containing KOH. The standard deviation is ± 0·05 per cent. G. P. Cook

1278. **Kjeldahl method for organic nitrogen.** R. B. Bradstreet (*Anal. Chem.*, 1954, **26** [1], 185–187).—The applications of the Kjeldahl method to organic analysis since 1939 are reviewed. G. P. Cook

1279. **Determination of nitro nitrogen by the Kjeldahl method.** R. B. Bradstreet (*Anal. Chem.*, 1954, **26** [1], 235–236).—The effect of various aromatic hydroxy compounds on the conversion of nitro compounds to a more easily reducible form is studied. The results obtained indicate that a mixture of equal parts of 1-naphthol and pyrogallol gives the best results. The effect of using a larger amount of K_2SO_4, with consequent increase of the digestion temp., was also studied and results show that the use of 18 g of K_2SO_4, instead of the conventional 10 g, gives improved recoveries of N, when used with 5 g of $Na_2S_2O_3$. G. P. Cook

1280. **Analysis of organic compounds containing fluorine.** R. Belcher (*Chim. Anal.*, 1954, **36** [3], 65–67).—In an interim progress report on the development of reliable methods for analysing fluorocarbons, chlorofluorides, and so on, it is claimed that C and H are estimated best by combustion of the sample at 900° C with absorption of SiF_4 on a layer of NaF at 270° C. Provided certain precautions are observed, F may be estimated by heating the sample at $\simeq$ 650° C with Na or K in a nickel bomb and subsequently weighing the PbClF formed (for samples $\lesssim$ 25 mg) or titrating with $Th(NO_3)_4$ (for samples $<$ 25 mg). Traces of H are estimated (to $\pm$ 0·005 per cent.) by a procedure based on the decomposition of 200 mg of the compound in a platinum tube at 1300° C, followed by absorption and acidimetric titration of HF in H_2O. In estimating the other halogens, the sample is decomposed in the nickel bomb with Na, a pellet of solid CO_2 followed by drops of distilled H_2O being added to destroy the metal within 2 min. I, Br and Cl are estimated in aliquots of the washings from the bomb; standard methods are used for I and Br and the $HgO.Hg(CN)_2$ method for small amounts of Cl. A method of estimating Cl, Br and I together in the washings is also described; it involves separate estimations of (*i*) I (by the Leipert reaction), (*ii*) I + Br (by oxidation with NaOCl) and (*iii*) total alkalinity (with 0·01 *N* H_2SO_4), which can be determined because $HgX_2.Hg(CN)_2$ (where X is a halogen atom) is formed under the specific operating conditions. A compensatory titration with 0·01 *N* H_2SO_4 is finally made to find the amount of Cl′ present. The estimations of N and S are being studied. W. J. Baker

1281. **Determination of hydrocarbon classes by chromatography with visual and fluorescent indicators.** P. G. Harvey and R. M. Pearson (*Analyst*, 1954, **79**, 158–163).—A method is described for the determination of hydrocarbon classes in petrol, light-petroleum distillates, etc., by adsorption on silica gel and use of indicators to mark the boundaries between the aromatics and olefines and between the olefines and saturated hydrocarbons. The visual indicators are bis-diphenylene-ethylene (prep. described) and carotene. Two indicators fluorescent in u.v. light are extracted from Trinidad asphalt. The oil sample is placed in a specially constructed tube terminating in a length of 2-mm diam. precision-bore tubing. The tube is packed with silica gel and a portion of the gel containing the marker indicator is located in the upper part of the precision tubing. The sample (0·5 ml) is run on to the gel, a further amount of gel is superimposed on to which alcohol is run and then pressure is applied to the upper part of the tube. When separation is complete the aromatic and non-aromatic zones are visible in the fine tube and can be measured and related to the length of the total sample zone. The procedure with fluorescent indicators differs only in addition of the indicators to the sample and measurement of the zones in u.v. light.

A. O. Jones

1282. **Use of molybdates for estimating the amount of olefinic-type hydrocarbons in air.** R. D. Macphee (*Anal. Chem.*, 1954, **26** [1], 221–225).—Micro-quantities of olefinic hydrocarbons in air are determined by utilising the gradual colour change from yellow to green accompanying reduction of complex and simple molybdates in acid media; this is analogous to a method of determining carbon monoxide in air. The approximate amount of C_3 and heavier olefines can be determined and application to air-pollution work is suggested. The proposed molybdate reagent made by mixing 6·1 g of sodium molybdate with 25 ml of distilled H_2O, 0·35 ml of $PdSO_4$ (aq. 10 per cent.), 40 ml of glacial acetic acid and 40 ml of conc. H_2SO_4 is nearly equally sensitive, on a weight basis, to all olefines, and is not influenced by aromatic or saturated compounds. Variation of the palladous sulphate or the sodium molybdate contents of the reagent alters the sensitivity for straight-chain olefines with respect to cyclic and branched-chain olefiines.

D. R. Glasson

1283. **Determination of copper acetylides in presence of other copper compounds.** N. N. Polyakov (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 302–305).—CuC_2 and Cu_2C_2 do not yield their equivalents of C_2H_2 on treatment with dil. HCl, but yields of C_2H_2 are stoicheiometric on treating the compounds with KCN soln. The C_2H_2 can be absorbed in ammoniacal Cu_2Cl_2 soln. and the pptd. $Cu_2C_2.H_2O$ can be determined iodimetrically.

G. S. Smith

1284. **Purity tests on benzene by measurements of dielectric constant and of infra-red absorption.** R. Mecke and K. Rosswog (*Angew. Chem.*, 1954, **66** [3], 75–78).—Even when the contaminant is non-polar, measurements of dielectric constant (ϵ) of benzene give as good indications of the amount of impurity as those of density, refractive index, u.v. and i.r. absorption. The variation of ϵ during the drying of benzene in the Schupp and Mecke apparatus is recorded. R. C. Murray

1285. **Xyloles.** British Standards Institution (B.S. 458:1953, 37 pp).—This revised edition of B.S. 458:1939 completes the series of the four British Specifications for benzoles and allied products—the other three already published in 1953, being "B.S.135. Benzoles"; "B.S.479. Coal Tar Naphthas"; and "B.S.805. Toluoles." Whereas the 1939 Standard gave specifications for xyloles of three boiling ranges, *viz.*, 2°, 3° and 5°, the revised standard in addition includes two grades of 10° xylole; low gravity xyloles of 3°, 5° and 10° range; and two 3° and 5° solvent xyloles which have received less drastic sulphuric acid treatment than normal. Methods for testing these nine grades are fully described. An improved method is given for determination of corrosive sulphur by which the copper strip is further treated to produce H_2S stain on Pb acetate paper. By matching on a Lovibond comparator this test is placed on a quantitative basis. D. Jenkins

1286. **Dispersion methods of determining aromatic hydrocarbons in mixtures with hydrocarbons of other classes. Analysis of mixtures not containing unsaturated compounds.** B. A. Kazansky, M. I. Rozengart, O. D. Sterligov and G. A. Tarasova (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 245–252).—Several dispersion methods of determining aromatic hydrocarbons in mixtures with other hydrocarbons are discussed, and a method not requiring determinations of sp. gr. or correction for non-additivity is recommended. The calculation with binary mixtures is made by means of the formula—

$$\omega_R = \left[\left(\frac{n^2_F - 1}{n^2_F + 2} - \frac{n^2_C - 1}{n^2_C + 2}\right) \Big/ (n_D - 1)\right] \times 10^3$$

where ω_R is the relative dispersion, and n_F, n_C and n_D are the refractive indices for the H lines F and C, and the Na line D. G. S. Smith

1287. **The analysis of γ-hexachlorocyclohexane [gamma-benzene hexachloride].** S. Wolf, C. Münster and E. Sarfert (*Z. anal. Chem.*, 1953, **140** [1], 25–40).—Methods for the determination of γ-benzene hexachloride (**I**) are shortly reviewed. Those which can be carried out in an ordinary industrial laboratory are selected for detailed study. Polarographic determination is extensively discussed. A method enabling estimations to be carried out at room temp. without thermostat and maximum supressors is described. Difficulties due to simultaneous reduction of $C_6H_5Cl_7$, $C_6H_4Cl_8$ at the dropping-mercury cathode are overcome. Over the most suitable range (5 to 90 per cent.), **I** can be determined with an accuracy of ± 3 per cent. A refractive index method is proposed for rapid routine control of mixtures consisting chiefly of α- and γ-isomers. Glass of suitable n_D (*e.g.*, 1·5101) is powdered and mixed with the sample; the mixture is heated on a Kofler heating bank and the temp. at which glass becomes invisible gives from a suitable calibration graph the γ-isomer content. A dielectric constant method is proposed for routine analysis of a large number of samples. The change in the dielectric constant of chlorobenzene when the sample is dissolved in it is measured. If the content of α-isomer is more than 70 per cent., the method cannot be used. The β-isomer, if present, is separately estimated and corrected for. Accuracy over the range 30 to 100 per cent. is ± 3 per cent. The combination of the refractive index and dielectric constant methods satisfies normal requirements of industry.

P. S. Stross

1288. **The determination of gamma isomer in crude benzene hexachloride by a carbon-14 isotope-dilution method.** R. Hill, A. G. Jones and D. E. Palin (*Chem. & Ind.*, 1954, [6], 162–163).—The sample of crude benzene hexachloride was mixed in soln. with pure radioactive gamma isomer of known activity, the dilution ratio being such that the gamma fraction subsequently separated (by extraction, paper chromatography and crystallisation) had about one-hundredth of this activity. Activity assays were made on barium carbonate, thick spacing with 15 to 20 mg of $BaCO_3$ per sq. cm being used. Counting was on a methane-flow proportional counter. The validity of the method is dependent upon the purity of the active material and the diluted sample; the precision was ± 3 per cent.

M. Tadman

1289. **Determination of Dichlorophene, Hexachlorophene and 2:2′-thiobis-(4:6-dichlorophenol) in soap and cosmetic preparations.** J. E. Clements and S. H. Newburger (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 190–197).—A soap soln. is acidified and extracted with $CHCl_3$, which is then evaporated, the residue being dissolved in light petroleum, which is then extracted with methanol. The methanolic solution, after dilution and acidification, is extracted with *iso*propyl ether, which is then extracted with alcoholic NaOH. The solution is extracted with ethyl ether, which is evaporated and the residue is dissolved in ethanol. Absorbancies are determined at 260, 288 and 316; 270, 300 and 330; and 262, 308 and 354 mμ, for Dichlorophene, Hexachlorophene and 2:2′-thiobis-(4:6-dichlorophenol), respectively. In tests of the method, recoveries of 97·4 to 100·2, 93·2 to 98·6, and 96·2 to 97·6 per cent., respectively, of these added materials were attained.

A. A. Eldridge

1290. **Analysis of cyclohexanone.** A. Castiglioni and G. Bionda (*Z. anal. Chem.*, 1954, **141** [1], 38–39).—Condensation products of *cyclo*hexanone (1 mol) with piperonylaldehyde (2 mol) or anisaldehyde (2 mol) are recommended as suitable for the gravimetric determination of *cyclo*hexanone. Pptn. is carried out in alkaline alcoholic soln. and after 12 hours the 2:6-dipiperonylidene- or 2:6-dianisylidene-*cyclo*hexanone is washed in water, dried at 100° C and weighed.

C. G. Taylor

1291. **Bromimetric estimation of compounds with two carbonyl groups in the α- or β- position. Influence of mercuric sulphate.** J. Modiano and J.-C. Pariaud (*Bull. Soc. Chim. France*, 1954, **21** [2], 189–191).—Aliphatic α-diketones and other compounds containing adjacent : CO groups (diacetyl, dibutyryl, oxalic acid, and so on) in ethanol or acetic acid soln. are oxidised quant. by excess of aq. Br only provided that 10 to 20 ml of 0·2 *N* $HgSO_4$ are present to raise the oxidation potential. After the reaction (*in vacuo*) is complete, 10 ml of 3 *N* NaCl soln. followed by 20 ml of 20 per cent. KI soln. are added and the liberated I is titrated with 0·1 *N* $Na_2S_2O_3$. In aq. soln. or presence of $HgSO_4$, β-diketones under similar conditions are dibrominated and can be estimated potentiometrically or by direct titration with 0·1 *N* bromate-bromide soln. if rapidly enolisable, *e.g.*, acetylacetone or dimedone, or by adding an excess of dimedone and titrating the excess of Br by means of KI and $Na_2S_2O_3$ if enolisation takes ¾ to 2½ hr., *e.g.*, ethyl acetoacetate or ethyl benzoylacetate When analysing a mixture of α- and β-diketones, $HgSO_4$ must be present and NaCl should be added before the dimedone; the α-diketone is estimated separately as above and the β-diketone content is found by difference. The mechanism of the reaction and the applicability of the method for any particular diketone are discussed briefly. The precision is ± 1 per cent.

W. J. Baker

1292. **New techniques for adding organic acids to silicic acid columns.** V. Zbinovsky and R. H. Burris (*Anal. Chem.*, 1954, **26** [1], 208–210).—A method is described for successfully introducing organic acids or their Na salts in the aq. phase into silicic acid columns and eliminating dehydration of the silicic acid. The acids and salts can also be introduced as a uniform narrow band by adding them in blotter discs. Results are best when the column is prepared with the max. quantity of water and when the aq. sample introduced is as small as possible. The recoveries of added acids after separation are 90 to 100 per cent.

G. P. Cook

1293. **Polarographic determination of citric acid. Polarography of pentabromoacetone.** P. J. Elving and R. E. van Atta (*Anal. Chem.*, 1954, **26** [2], 295–298).—A brief review of methods of determining citric acid is given, followed by an investigation of the polarographic method. The citric acid is converted into pentabromoacetone by the procedure of Hargreaves, Abrahams and Vickery (*Brit. Abstr. C*, 1951, 304), and then determined polarographically. The polarographic characteristics of pentabromoacetone were first investigated and it was found that in the region of pH > 7, three waves appeared, both in aq. NH_3 buffers at pH 8·2, 8·8 or 9·5 and in phosphate buffers at pH 10·5, 11·5 or 12·5. Although these waves appeared to be independent of pH, the $E_{\frac{1}{2}}$ of each of the three waves was different for the two types of buffer

solution. Finally the aq. NH_3 buffer at pH 8·8 was selected as giving the best results. Manganese is introduced into the solutions during the conversion of the citric acid to the ketone, and allowance has to be made for its effect on the ketone polarogram. Details of the method of measurement of the wave heights are given. Three waves were observed in the polarography of pentabromoacetone and they are apparently due to dibromoacetic acid and bromoform into which the ketone is quant. hydrolysed. D-*iso*Citric acid can also be determined by this method after conversion first to citric acid and then to the ketone.

B. LAMB

1294. **New colour reactions for oxalates and sulphites.** A. P. Kreshkov, S. S. Vilborg and K. I. Filippova (*J. Anal. Chem., U.S.S.R.*, 1953, **8** [5], 306–310).—Characteristic brown crystals are given by the reaction of oxalates and sulphites with benzidine in presence of Cu^{++} salts. The compounds are salts of a complex $[Cu\{C_{12}H_8(NH_2)_2\}_n]^{++}$. With a reagent composed of equal vol. of 0·5 per cent. benzidine in 5 per cent. acetic acid and 0·2 *N* Cu acetate the sensitivity for oxalate corresponds to 0·15 mg in 1 ml when the reaction is carried out in a test tube and to 20 μg in 1 drop on a spot plate.

G. S. SMITH

1295. **Circular-paper chromatography. VIII. Separation, identification and quantitative estimation of sugars and oligosaccharides.** K. V. Giri and V. N. Nigam (*J. Indian Inst. Sci., A*, 1954, **36** [1], 49–62).—Solutions of sugars are spotted at the centre of large circular filter-papers, the papers are dried at room temp., and a developing soln. is applied at the centre as described by Giri and Rao (*Nature*, 1952, **169**, 923). The most suitable developing solutions are *n*-butanol - acetone - H_2O (20:70:10) and *n*-butanol - pyridine - H_2O (60:40:30). R_F values are given for 22 sugars in these solvents and in *n*-butanol - acetic acid - H_2O (40:10:50). A second development after drying improves separation. The positions of the sugars are identified by brushing the paper with the following reagents: aniline - diphenylamine - H_3PO_4 (bands coloured according to the nature of the sugar), 1-naphthylamine - H_3PO_4 (yellow bands with ketoses), aniline hydrogen phthalate (different colours for aldohexoses and aldopentoses), or triphenyltetrazolium chloride (**I**) (red bands with reducing sugars). The chromatogram may be divided into sectors, and each sector is brushed with a different reagent; the colours are more easily differentiated in u.v. light. The bands obtained with **I** and reducing sugars are dried slowly, and cut out, and the red colour is extracted with ethanol; the sugars can then be determined colorimetrically to within ± 5 per cent. by comparison with the bands obtained in an adjoining sector with a standard solution of the sugar. By use of thick paper and multiple development, 1 ml of soln. containing 10 mg of each of 10 sugars could be resolved. The method is applicable to analysis of carbohydrates in urine or blood.

H. P. PAGET

1296. **A dipping technique for revealing sugars on paper chromatograms.** G. Harris and I. C. MacWilliam (*Chem. & Ind.*, 1954, [9], 249).—The conventional benzidine - trichloroacetic acid, naphtharesorcinol - phosphoric acid and diphenylamine - aniline - phosphoric acid reagents are modified by replacing ethanol by acetone and reducing the amount of water.

M. TADMAN

1297. **Chromatographic separation of methylglucoses.** W. J. Whelan and K. Morgan (*Chem. & Ind.*, 1954, [3], 78).—By means of the charcoal column technique described previously (Whelan *et al.*, *J. Chem. Soc.*, 1953, 1293) with an artificial mixture of partly methylated glucoses it is found that the greater the number of methoxyl groups in the glucose mol. the higher is the concn. of ethanol required to elute them and that the difference is sufficient to enable an absolute separation to be made of di-, tri- and tetra-methylglucoses.

J. M. JACOBS

1298. **Optical and crystallographic properties of sucrose hemiheptahydrate.** F. T. Jones and F. E. Young (*Anal. Chem.*, 1954, **26** [2], 421).—Crystals of sucrose hemiheptahydrate are obtained by slow growth at − 7·5° C in a slightly supersaturated aq. soln. Optical and crystallographic properties are tabulated.

J. DAVIS

1299. **Determination of total and primary hydroxyl in cellulose esters by ultra-violet absorption methods.** C. J. Malm, L. J. Tanghe, B. C. Laird and G. D. Smith (*Anal. Chem.*, 1953, **26** [1], 188–190).—In the determination of total and primary hydroxyl content in cellulose esters, ultra-violet absorption at 280 and 259 mμ gives a measure of the quantity of carbanilate (phenylcarbamate) and trityl (triphenylmethyl) introduced into hydrolysed cellulose acetate by reaction with phenyl *iso*cyanate and trityl chloride, respectively. The phenyl *iso*cyanate reaction for total hydroxyl is conducted at 100° C in pyridine soln., the excess of *iso*cyanate being removed by pptg. and washing the product in ethanol. The trityl chloride reaction for primary hydroxyl when conducted in pyridine soln. takes 24 hr. The standard deviations for a single value are ± 0·020 per cent. for a mean total hydroxyl content of 3·026 per cent., and ± 0·03 per cent. for a primary hydroxyl content of 1·134 per cent.

G. P. COOK

1300. **Interference of inorganic salts in the chromatography on paper of amino-alcohols, diamines and diamino-acids.** D. M. Waldron-Edward (*Chem. & Ind.*, 1954, [4], 104–106).—Data are presented that show that, under certain conditions, trace amounts of SO_4'' interfere in the paper chromatography of certain amino compounds. Addition of as little as 5 to 50 μg of SO_4'' results in a marked decrease in the R_F values of these amino compounds when paper chromatograms are developed in neutral or mildly acidic or basic solvents. In strongly acidic or basic solvents no interference occurs. Ions other than SO_4'' that do not migrate, or migrate very slowly, in mildly acidic or neutral solvents, retard the migration of these amines in a similar way. It is suggested that this phenomenon could be used to separate diamines, diaminocarboxylic acids and glucosamine from mono-amines and mono-amino-acids by addition of minute quantities of Na_2SO_4 to a mixture before chromatography on paper.

J. M. JACOBS

1301. **Studies in spectroscopy. VI. Ultra-violet and infra-red spectra of nitrosamines, nitrites and related compounds.** R. N. Haszeldine and J. Jander (*J. Chem. Soc.*, 1954, 691–695).—Both u.v. and i.r. spectra enable nitrosamines and nitrites to be distinguished from related compounds. Nitrosamines are characterised by a low intensity maximum at ≃ 365 mμ and a high intensity maximum at 235 mμ. Unlike nitrosamines, nitrites

have identical spectra in light petroleum and ethanol, and show multiple absorption in the 310 to 400-mμ region. In the i.r. region nitrites are characterised by 4 strong bands at 5·8, 6·1, 6·2 and $\simeq$ 12·5μ. Nitrosamines are characterised by bands at 7·1 to 7·4 μ, $\simeq$ 8 μ and $\simeq$ 9·5 μ. D. LIFF

1302. **Polarography of certain organic polysulphides.** J. H. Karchmer and M. T. Walker (*Anal. Chem.*, 1954, **26** [2], 271–280).—The polarography of dibenzyl, di-*n*-butyl and di-*tert.*-butyl trisulphides and corresponding tetrasulphides has been compared with that of the related disulphides in a supporting electrolyte solvent of benzene-methanol, made 0·1 *N* with respect to Na acetate and acetic acid all these tetrasulphides and the dibenzyl trisulphide produce three polarographic waves with a dropping-mercury cathode. The $E_{\frac{1}{2}}$ of these waves varies with the substituent hydrocarbon groups and with the number of S atoms present, but they are sufficiently similar to each other and unique with respect to the polarograms of other substances to be analytically useful. The first wave, which occurs fairly early in the potential scale $-$ 0·3 to $-$ 0·7 V *vs.* the S.C.E., its exact voltage depending upon the compound being examined, cannot be used quant. since the wave height is not linear with concn. above 8 $\times$ 10^{-2} millimolar, while the second step (which always shows a large maximum) does not appear at concn. below this. The polarograms are further complicated by the wave for elemental sulphur, which is sometimes present in the natural polysulphide. There is also evidence that the current is not entirely diffusion controlled and a calibration curve must be drawn for each particular application. Polarograms were also taken in tetra-*n*-butylammonium hydroxide, the waves being somewhat different in shape in this medium. Full details of the procedure and preparation of the various compounds are given in detail, but it is pointed out that in order to obtain quant. results three polarograms must be run—two concentrations of the polysulphide material in acetate base and one in the quaternary base. Most of the work done was at concn. of 5 $\times$ 10^{-2} millimoles, but calibration figures are given for 0·1 millimoles to 1·0 millimoles. B. LAMB

1303. **Gravimetric determination of tetramethylphosphonium ion. Use of chloroplatinic acid as precipitant.** C. J. Anderson and R. A. Keeler (*Anal. Chem.*, 1954, **26** [1], 213–214).—In the method, which is based upon the insolubility of tetramethylphosphonium chloroplatinate in ethanol, the sample in the chloride form is treated with an excess of chloroplatinic acid and evaporated to small bulk, the residue being extracted with ethanol, filtered and weighed after washing and drying. NH_4^+, K^+, Rb^+ and Cs^+ interfere, but moderate amounts of Ca, Sr and Mg chlorides can be tolerated. The accuracy is > 99·6 per cent. and the precision is 2 parts per thousand. An ion-exchange method for the separation of tetramethylphosphonium ion from anions is also included. G. P. COOK

1304. **The use of paper chromatography for the study of hydrogenation reactions.** W. Irion and E. Moosmüller (*Z. anal. Chem.*, 1953, **140** [6], 416–421).—The course of hydrogenations can be closely followed by running two identical paper chromatograms and spraying one with ninhydrin and the other with bromophenol blue or bromocresol green. Examples given are the hydrogenation of the ethyl ester of 5-cyanomethylfuran-2-carboxylic acid and the catalytic hydrogenation of 5-nitro-3-oxo-*n*-hexanoic acid under various conditions. The amounts of primary and secondary amines as well as de-amination products produced in the reaction can be followed easily. P. S. STROSS

1305. **The semimicro-determination of the benzoyl group.** E. V. Schivizhoffen and H. Danz (*Z. anal. Chem.*, 1953, **140** [2], 81–88).—The determination in non-aqueous medium of the benzoic acid obtained by saponification of the benzoyl group is described. H_2SO_4 (50 per cent. v/v), NaOH (5 *N*), or sodium ethoxide (2 g of Na per 100 ml of ethanol), the last two with pyridine, is used for the hydrolysis, which takes 4 to 5 hr. The benzoic acid is extracted with chloroform and is titrated in dimethylformamide soln. with 0·05 *N* sodium methoxide (thymol blue). The analysis can be done on a 50 to 100-mg sample with an average error of $\pm$ 0·2 per cent. P. S. STROSS

1306. **Recording Raman spectrometry in the analysis of petroleum products.** L. Robert (*Spectrochim. Acta*, 1953, **6** [1], 115–123).—An adaptation of a spectrograph to take a photo-multiplier tube assembly that scans a range of 60 mμ is described. The source of exciting radiation is an a.c. mercury vapour lamp; the 4358 A line is used. The sensitivity is given as the mean fluctuation of response divided by the actual response for the 459 cm^{-1} line of CCl_4; for this instrument it is 0·01. The intensities of lines from pure substances are related to this line in calibration. In analysis of petrol fractions, the results for alkanes are inferior to those by i.r. measurements, but aromatics can be determined without dilution and percentage of aromatics and alkenes can be determined on a total petrol. An attempt to use the 5461 A line for excitation with fluorescent material showed that the photo-multiplier tube is not highly sensitive in this region. The method is also used for aq. solutions of *iso*propanol and acetone, which are not amenable to i.r. measurement without removal of water. E. J. H. BIRCH

1307. **Analysis of petrols by infra-red spectrometry.** J. Favre (*Spectrochim. Acta*, 1953, **6** [1], 98–109).—Straight-run petrols containing no alkenes are distilled up to 150° C to give eight fractions and a residue, which are then analysed. From the higher-boiling fractions, aromatic hydrocarbons can be removed by silica-gel absorption, enabling $\cdot CH_3$, $:CH_2$ and $\vdots CH$ groups to be determined in the compounds of higher mol. wt. by a method of calculation from the i.r. absorption. Suitable absorption bands and distillation limits are quoted for the determination of 22 alkanes, 12 *cyclo*alkanes and 6 aromatic hydrocarbons. For alkenes, the possible methods of analysis are discussed and the analysis is effected by distilling eight fractions and determining aromatics as before. These values are then used for correcting the absorption of the alkenes in the α, β-*trans*- and $\alpha\beta$- groups, the absorption being related to the mol. wt. characteristic of the fraction. The alkanes and *cyclo*alkanes are determined after treatment of the alkenes with H_2SO_4. Extension of the method to β-*cis*- and $\beta\beta$-alkenes seems to be valid. The time for spectrometry and calculation up to the 100° C fraction for the alkanes is 6 hr., and for the classification of the alkenes 4 hr. E. J. H. BIRCH

1308. **Extraction and recovery of thiols from petroleum distillates.** R. L. Hopkins and H. M. Smith (*Anal. Chem.*, 1954, **26** [1], 206–207).—The qualitative testing and quantitative application of a method for separating thiols by means of 2 *N* Na aminoethoxide in anhydrous ethylenediamine soln. is described. Soluble aromatics are removed by washing the extract with *iso*pentane. The thiols are quantitatively recovered by acidifying the soln. containing the Na salts and steam-distilling it. Successful separation of thiols from a distillate boiling between 111° and 150° C is reported. The thiols are best concentrated by adsorption on alumina before extraction.

D. R. GLASSON

1309. **The infra-red spectra of some unsulphonated mono-azo dyes.** M. Dolinsky and J. H. Jones (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 197–209).—The i.r. spectra of 31 unsulphonated azo dyes and related compounds are given. The absence of characteristic peaks in the 3-μ and 6-μ regions indicates a zwitterion structure for the *o*-hydroxyazo compounds.

A. A. ELDRIDGE

1310. **Dichlorofluorescein as an indicator in the determination of anionic detergents.** H. Iwasenko (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1165–1169).—It is recommended that the concn. of the standard (quaternary ammonium chloride) cationic detergent soln. used in the procedure should be 0·004 *M*, and that dichlorofluorescein should be used as indicator (*Trans. Faraday Soc.*, 1948, **44**, 226).

A. A. ELDRIDGE

See also Abstracts 1190, 1438.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

1311. **Quantitative determination of reducing sugars by paper chromatography and its application to the micro-determination of blood sugar.** K. Wallenfels, E. Bernt and G. Limberg (*Angew. Chem.*, 1953, **65**, 581–586).—Of six reagents for direct photometry of reducing sugars, developed by butanol - pyridine - water on a paper chromatogram, ammoniacal $AgNO_3$ soln. was the most sensitive when the area of the spots was the criterion. This sensitivity is high only when the spots are developed by quick drying of the paper after spraying, and then heating in a current of steam at 100° C for 10 sec.; the background paper is then not darkened much, and coloration is removed altogether on washing the chromatogram. The graph of spot area against μg of glucose present is then a straight line from 6 μg up to 50 μg, and photometric measurements are nearly proportional. Some results are also given for lactose and lactotriose and for mixtures of sugars obtained during the hydrolysis of lactose by mould lactase. A wider range of accurate determination is possible by the use of triphenyltetrazolium chloride as spraying reagent, with which reducing sugars give the red formazans. The reaction is less temp. sensitive; 75° C is most suitable, as different sugars then react equally well. The paper of the chromatogram also reacts and the blank value per sq. cm must be carefully determined. Portions of paper containing the spots are then cut out, weighed and extracted. The colour intensity is determined at 546 mμ in a 1-cm layer. The colour formation is affected by light and temp., so that the reaction must be carried out in diffuse light in a relatively darkened room and at a constant heating temp. (75° C). The variations are shown in graphs. Some results are given for blood sugar analyses.

SUGAR IND. ABSTR.

1312. **Determination of blood-sugar according to Hagedorn - Jensen, and observations concerning insulin.** M. Herter (*Arch. Pharm., Berlin*, 1954, **287** [2], 63–65).—After removal of the proteins by means of $Zn(OH)_2$, centrifugation and subsequent filtration through filter-paper (Schleicher and Schüll No. 587 E) is preferable to filtration through cotton-wool only. In preparation for the iodimetric titration, the soln. of KI, $ZnSO_4$ plus NaCl, acetic acid and starch are mixed (instead of being added separately) and decolorised by means of 0·005 *N* $Na_2S_2O_3$ before use. Ethanol in the amounts likely to occur in blood does not interfere with the determination.

P. S. ARUP

1313. **Determination of alcohol in blood and urine. A survey of a report made by a Panel of Analysts appointed to assist the Committee of the British Medical Association on alcohol and Road Accidents in their report "Recognition of Intoxication."** Presented on behalf of the Panel by D. W. Kent-Jones and G. Taylor (*Analyst*, 1954, **79**, 121–133).—Two methods are suggested as suitable official methods for forensic purposes without prejudice to the accuracy and reliability of other methods. These are an amended micro-method of Cavett (*Brit. Abstr. A III*, 1938, 756) and the macro-method of Kozelka *et al.* (*Brit. Abstr, A III*, 1942, 427). Both methods depend upon the reduction of acidified $K_2Cr_2O_7$ by the alcohol and are described in full detail. The procedures must be followed exactly and the apparatus must be thoroughly clean. The results of inter- and intra-laboratory collaborative work are quoted and statistically analysed. The Cavett method does not appear to have any systematic error whereas the method of Kozelka *et al.* is more precise but gives slightly low results.

A. O. JONES

1314. **A simple difference-method for the estimation of serum calcium by flame photometry.** H. J. Hübener, H. Maurer and T. Walther (*Klin. Wschr.*, 1953, **31**, 1095–1096).—Three solutions are prepared as follows: (*a*) 2 ml of the serum sample and 2 ml of 0·5 *N* HCl are made up to 20 ml with distilled water; (*b*) 2 ml of the serum and 2 ml of acid $CaCl_2$ soln. (8 mg $CaCl_2$ per 100 ml of 0·5 *N* HCl) are made up to 20 ml with distilled water; (*c*) 2 ml of the acid $CaCl_2$ soln. are made up to 20 ml with distilled water. The Ca concn. of the three soln. are determined in a flame photometer and the Ca value for (*a*) is corrected for protein and other interferences by the factor $c/(b - a)$. Figures are given to show the significance of this correction factor in the estimation of Ca in human serum.

G. W. CAMBRIDGE

1315. **An improved technique for uropepsin assay.** J. D. Duffin and K. Kowalewski (*J. Lab. Clin. Med.*, 1954, **43** [1], 165).—The haemoglobin tyrosine technique (Mirsky *et al. J. Clin. Invest.*, 1948, **27**, 818) for uropepsin assay suffers from reduction in sensitivity when the urine contains

much chromogenic material, mainly phenolic compounds. A simple dialysis technique is presented for ridding the urine of interfering matter without loss of enzyme. N. E.

1316. **Improved method for determination of urinary 17-ketosteroids.** M. Masuda and H. C. Thuline (*J. Clin. Endocrinol.*, 1953, **13**, 581–586).—Interfering chromogens can be separated from the 17-ketosteroid fraction if the latter is dissolved in amyl acetate after development of the Zimmermann colour. P. C. WILLIAMS

1317. **Separation of 17-ketosteroids in 24-hour urine samples.** B. L. Rubin, H. Rosenkrantz, R. I. Dorfman and G. Pincus (*J. Clin. Endocrinol.*, 1953, **13**, 568–580).—A method of separating 17-ketosteroids by using the adsorption of the neutral, ketonic, digitonin-soluble steroids on silica-gel is described. The 17-ketosteroids in the eluates were sometimes identifiable by comparison with pure steroids, by infra-red analysis or by paper chromatography. There are 9 peaks among the eluates, 3 of which are considered to be artefacts. The major peaks are composed of androsterone and aetiocholane-3(α)-ol-17-one which constitute 60 per cent. of the whole; differentiation of the two varies with their relative proportions. The values obtained in 12 normal specimens are compared with those obtained by the $Al(OH)_3$ adsorption procedure. P. C. WILLIAMS

1318. **Chromatographic investigation of the amino-acid constituents of normal urine.** W. H. Stein (*J. Biol. Chem.*, 1953, **201** [1], 45–58).—A chromatographic technique previously described (*Brit. Abstr. C*, 1952, 62), in which columns of Dowex-50 ion-exchange resin are used, has been applied to normal urine. Quant. values have been obtained for taurine, threonine, serine, asparagine, glycine, alanine, amino-adipic acid, cystine, valine, *iso*leucine, leucine, tyrosine, phenylalanine, histidine, methylhistidine and lysine. N. E.

1319. **The use of cellulose as an adsorbent for the proteins of plasma in aqueous solution.** H. Brandenberger (*Helv. Chim. Acta*, 1954, **37** [1], 97–103).—Fibrinogen is retained quant. by colums of cellulose. Isolated albumin and an α_1-acid glycoprotein are not adsorbed, but γ-globulins obtained by alcohol-salt fractionation are partially adsorbed, indicating a change during isolation or storage. Some aspects of the paper chromatography of plasma proteins are discussed. D. LIFF

1320. **Action of copper on peroxidase reagents.** G. Curli (*Ann. Chim., Roma*, 1953, **43** [10], 670–678).—A comparison of the reaction of various peroxidase (**I**) reagents with Cu and with **I** derived from blood, urine and milk reveals differences in the reactions, particularly of Meyer's, Storch's and Leibowitz's reagents to Cu and to **I**, sufficient to eliminate the need for blank tests. R. C. MURRAY

1321. **Anthrone reaction in the determination of carbohydrates.** F. Grande, A. Utrera and J. C. de Oya (*Rev. Clin. Esp.*, 1953, **51**, 17–23).—Application of the anthrone reaction to the determination of glucose, pentoses and glycogen has been investigated. It appears that the reaction is due to condensation of anthranol with methylfurfural or hydroxymethylfurfural. D. F. COLE

1322. **Chromatography of pyruvic acid and of acetoacetic acid as their 2 : 4-dinitrophenylhydrazones.** S. Markees (*Biochem. J.*, 1954, **56** [4], 703–704).—It is confirmed that pyruvic acid 2 : 4-dinitrophenylhydrazone yields two spots, R_F 0·36 and 0·57, on paper strips (butanol - NH_3 - H_2O solvent). Acetoacetic acid yields an intermediate spot, R_F 0·48, which does not usually cause interference in blood analysis as, unless acetoacetic acid is present in high concentration, acetone 2 : 4-dinitrophenylhydrazone, R_F 0·94, results from the usual analytical procedure. J. M. SEARLE

1323. **A modified photometric ninhydrin method for the analysis of amino- and imino- acids.** W. Troll and R. K. Cannan (*J. Biol. Chem.*, 1953, **200** [2], 803–811).—It is claimed that, by the proposed procedure, the theoretical colour is given with 10 naturally occurring amino-acids at room temp. and with all except tryptophan and lysine at 100° C. Hydroxyproline in the presence of other amino-acids was estimated photometrically after extraction of a red derivative from the reaction system with benzene. This pigment is a precursor of the yellow compound, which is the final product of the reaction with ninhydrin. P. N. CAMPBELL

1324. **Ultramicro-determination of arginine by a compound microbiological assay method.** M. N. Camien and M. S. Dunn (*Proc. Soc. Exp. Biol. Med.*, 1954, **85** [1], 177–183).—The sensitivity of the microbiological method of assay for arginine can be compounded by using a secondary microbiological assay to determine the D-lactic acid component of the products of the first assay. In this way the sensitivity is about 144 times that of the standard method. N. E.

1325. **Polarographic and amperometric mercurimetric determination of disulphide groups in cystine, oxidised glutathione and proteins.** W. Stricks, I. M. Kolthoff and N. Tanaka (*Anal. Chem.*, 1954, **26** [2], 299–303).—Complete hydrolytic disintegration of the protein into amino-acids as used in the conventional methods of disulphide determinations in biological materials can be replaced by a more rapid procedure involving pepsin digestion and partial hydrolysis in *M* HCl. A polarographic study of soln. containing cystine, reduced glutathione or oxidised glutathione in the presence of Na_2SO_3 and various concn. of Hg^{++} showed that the disulphide can be accurately titrated with $HgCl_2$ at the dropping-mercury electrode. The anodic diffusion current of cysteine in an alkaline soln. of an acid hydrolysed protein in the presence of $SO_3^{=}$ can be used for the direct determination of disulphide in protein. The final determination can be made in either borax or aq. NH_3 buffer soln. Full experimental details are given for the determination of disulphide in bovine plasma albumin after pepsin digestion and acid hydrolysis, and also for the mercapto content of undenatured protein at a rotating platinum electrode (*Anal. Abstr.*, 1954, **1**, 1326). B. LAMB

1326. **Amperometric mercurimetric titration of mercapto groups in biologically important substances at the rotated platinum-wire electrode as indicator electrode.** I. M. Kolthoff, W. Stricks and L. Morren (*Anal. Chem.*, 1954, **26** [2], 366–372).—By titrating with mercuric acetate in aq. media, ·SH in cysteine and reduced glutathione and

traces of ·SH in native and denatured proteins are determined. A rotating platinum-wire electrode is used as the indicator electrode. The method is rapid and accurate to ± 2 per cent. for ·SH contents between 7 and 50 μg. J. DAVIS

1327. **Quantitative determination of S-35-labelled compounds in complex mixtures.** J. B. Melchior and A. H. Goldkamp (*Anal. Chem.*, 1954, **26** [1], 233–235).—DL-Methionine-^{35}S is evaporated either in small aluminium dishes or in small plastic dishes lined with filter-paper. The radioactivity is determined for various amounts of methionine alone and mixed with $BaCl_2$, NaH_2PO_4 and Cu^{++}; the effects of self-absorption and added materials on the counting rate is discussed for the two techniques. Precision is claimed to be as good as for methods involving the isolation and determination of activity of $Ba^{35}SO_4$ or benzidine sulphate-^{35}S. D. A. PANTONY

1328. **Analysis of amino-acids present in biological material by chromatographic methods suitable for routine clinical use.** J. B. Paton and M. L. Wellby (*Med. J. Aust.*, 1953, **ii**, 639–644).—Methods for carrying out chromatographic analysis of biological fluids are described and results obtained in a variety of clinical conditions are recorded. W. W. HOLLAND

1329. **The isolation and estimation of the steroid oestrogens in placental tissue.** F. L. Mitchell and R. E. Davis (*Biochem. J.*, 1954, **56** [4], 690–698).—Existing chromatographic methods for separating oestrone, oestradiol and oestriol are examined, and a method for separating and purifying these oestrogens in placental tissue is described. Free, conjugated and protein-bound oestrogens are extracted with ethanol and separated chemically into oestriol and oestrone - oestradiol fractions. Extracts from 10 to 20 g of tissue, containing 0·5 to 20 μg of oestrogen, are then chromatographed on paper at 32° C. Solvents used are light petroleum, boiling at 100° to 120° C (stationary phase, methanol) for oestrone, R_F 0·2, and oestradiol, R_F 0·07, and benzene (stationary phase, 50 per cent. aq. methanol) for oestriol, R_F 0·13. The oestrogens are detected on the paper by spraying with Folin and Ciocalteu's reagent, followed by exposure to NH_3. The suitability of this reagent for detecting other steroids is also investigated. The oestrogens are determined fluorimetrically after elution with methanol and treatment with H_2SO_4. When corrections are applied for the large losses found during recovery experiments, previously reported values for oestrogens in placental tissue are shown to need revision. C. E. SEARLE

1330. **Determination of oximase.** K. Yamafuji and F. Yoshihara (*Enzymologia*, 1954, **16** [3], 161–166).—The effect of ketones and aldehydes upon the colorimetric estimation of oximase under various conditions is described. The alkali method (*Enzymologia*, 1952, **15**, 313) in which the oximes are determined almost quantitatively by oxidation with I in alkaline soln. gives good results when applied to oximase, provided that the concn. of the carbonyl compounds in the reaction mixture is $\simeq 10^{-3}$ *M* for acetone and CH_3CHO and 10^{-4} *M* for pyruvic acid. Comparison of the alkali method with the measurement of NH_2OH produced after acid hydrolysis shows that trans-oximation probably takes place, possibly to carbohydrates, and that the newly formed oximes are hardly determined by the alkali method. Thus it is desirable that superfluous acceptors of oxime groups, especially sugars, are eliminated from the reaction mixture by extraction of the enzyme with slightly acidified H_2O (pH 6). D. BAILEY

1331. **A colorimetric assay for xanthine oxidase in rat-liver homogenates.** G. Litwack, J. W. Bothwell, J. N. Williams, jun., and C. A. Elvehjem (*J. Biol. Chem.*, 1953, **200** [1], 303–310).—A colorimetric method for the estimation of xanthine oxidase activity, based on the determination of the disappearance of substrate, is described. Because of its greater specificity, this method has a marked advantage over the manometric method. Chilled livers from freshly-killed rats are homogenised with a Potter - Elvehjem homogeniser in KH_2PO_4 - Na_2HPO_4 buffer soln., pH 7·4, and strained through gauze. Aliquots of the homogenate are incubated in a water-bath at 37° C for 40 min., and buffer and 0·038 *M* xanthine soln. or water are added. Samples are taken every 30 min. and added to 40 per cent. Na tungstate and aq. H_2SO_4; the proteins are then centrifuged. To an aliquot of the supernatant liquid is added dil. Folin - Ciocalteu reagent (1 + 1) and the colour is developed by addition of saturated Na_2CO_3 soln. and measured with aid of a 600-mμ filter. Recoveries of added xanthine average 101 per cent. The depletion of liver xanthine oxidase by dietary means and the inhibition of the enzyme with 2-amino-6-formyl-4-hydroxypteridine have been observed by both the colorimetric and manometric methods. D. V. PARKE

1332. **Estimation of water in biological material.** O. Harth, W. Kreienberg and D. Mertz (*Klin. Wschr.*, 1953, **31**, 905–907).—To 6 ml of 94 per cent. ethanol add 0·4 ml or 400 mg of the substance to be tested. After shaking for 30 min., filter and titrate 2 ml of the ethanolic mixture with xylene until turbid in a constant-temp. bath at 20° C. There is a linear relationship between the water content and the amount of xylene required to cause turbidity. The method is claimed to have an accuracy of about ± 0·3 per cent. G. W. CAMBRIDGE

1333. **The destruction of organic matter.** G. Roche Lynch (*Analyst*, 1954, **79**, 137).—The communication embodies introductory remarks to two other communications (*Anal. Abstr.*, 1954, **1**, 1334 and 1355). Dry ashing is most satisfactory if no loss occurs up to 500° C and H_2SO_4 may be added in the later stages to remove halogens. The method is not applicable to As and Hg and since volatility of Pb is uncertain, wet ashing is preferable. In wet oxidation treatment with H_2SO_4 and HNO_3 with subsequent addition of HNO_3 is satisfactory for amounts of sample > 7 g. Biological material may leave yellowish matter interfering with subsequent colorimetric work. Urine presents some difficulties and nitrosyl sulphuric acid has been recommended to remove urea. Co-pptn. of Pb with $Ca_3(PO)_4$ and Ca oxalate has been used but there is some doubt that pptn. of Pb is complete. Hg requires special treatment *viz.*, acidic oxidation with $KMnO_4$ under refluxing conditions before co-pptn. with another metal by H_2S. With large amounts of biological material (*e.g.*, 150 g) treatment with HCl, water and $KClO_3$ is useful and applicable when the metal sought is Hg. A. O. JONES

1334. **The preparation of biological material for the determination of trace metals. II. Destruction of organic matter in biological material.** G. Middleton and R. E. Stuckey (*Analyst*, 1954, **79**, 138–142).—In the method described HNO_3 is the only reagent used in quantity. The material is evaporated with dil. HNO_3 containing 5 per cent. of H_2SO_4 and heated on a hot-plate (≯ 350° C) while there is visible change. The cooled residue is moistened with HNO_3 and re-heated, the process being repeated as often as necessary. Fuming HNO_3 may be required in the final stage to remove dark patches. If the final residue is insoluble in dil. acid, fuming with a little H_2SO_4 and dilution with water is necessary, or the residue may be digested with 5 per cent. NaOH soln. and then dissolved in HCl. The total vol. of HNO_3 used should be noted to allow for trace elements in the acid. In the first stage H_2SO_4 may be omitted if there is no danger of ignition of the residue.

A. O. Jones

1335. **Estimation of zinc in biological specimens. Determination of zinc-65.** T. E. Banks, R. Tupper, R. W. E. Watts and A. Wormall (*Nature*, 1954, **173**, 348–349).—Three methods are described for the determination of ^{65}Zn in animal tissue: (*i*) wet combustion with HNO_3 or H_2SO_4 - SeO_2 followed by liquid counting, (*ii*) extraction of the acid soln. of the tissue with $CHCl_3$ - dithizone—the Zn is extracted with dil. HCl and liquid counted; in this way, interference from other radio-isotopes is eliminated, but 3 to 5 per cent. of ^{65}Zn is lost—; and (*iii*) scintillation counting of the homogenised tissue or of a solution obtained as in method (*i*). Method (*iii*) is preferred to methods (*i*) and (*ii*) as sensitivity and stability are better.

C. G. Taylor

1336. **Estimation of zinc in biological specimens. Separation of radioactive zinc from cyclotron-irradiated copper.** R. Tupper and R. W. E. Watts (*Nature*, 1954, **173**, 349).—The Cu target after cyclotron irradiation is arranged as the anode in a cell containing 4 *N* H_2SO_4, and electrolysis is continued until most of the ^{65}Zn has entered into soln. The soln. is evaporated to dryness and the residue is dissolved in *n*-butanol containing 4 per cent. v/v of constant-boiling HCl. This soln. is transferred to a cellulose column and eluted with *n*-butanol - HCl mixture, when most of the ^{65}Zn is removed. The eluate is evaporated and the residue is dissolved in constant-boiling HCl to give substantially carrier-free ^{65}Zn.

C. G. Taylor

1337. **Assay of radio-iron and radio-silver in biological samples.** L. Cheong, G. C. Perri and L. M. Sharpe (*Anal. Chem.*, 1954, **26** [1], 242–243).—^{110}Ag and ^{55}Fe are separated by the cupferron extraction procedure. The separation was successfully applied to 10 mg of Fe of low ^{55}Fe activity and as much as $2{\cdot}13 \times 10^{-3}$ mg of Ag of high ^{110}Ag activity. The recoveries of ^{110}Ag and ^{55}Fe from various rat tissues were 97 to 102 per cent. and 92 to 104 per cent., respectively. The extraction procedure described yields extracts free of substances such as Ca and PO_4''', which interfere with the efficient electroplating of the ^{55}Fe.

G. P. Cook

1338. **Studies of sebum. IV. The estimation of squalene in sebum and sebum-like materials.** V. R. Wheatley (*Biochem. J.*, 1953, **55** [4], 637–640).—A method of estimating unsaturated hydrocarbons is described; it is applicable to small amounts (5 mg) of sebum and similar materials and gives an average recovery of 80 per cent. of added squalene. After saponification, a hydrocarbon fraction is isolated chromatographically and the unsaturated material therein is determined iodimetrically. The method can be used for the determination of squalene in sebum and other lipids provided that the presence of squalene is first established and that no other unsaturated hydrocarbons are present. Data on the Liebermann - Burchard reaction of squalene are recorded.

B. Viney

See also Abstracts 1349, 1350, 1391.

Drugs

1339. **The ultra-violet spectrophotometric assay of alkaloids. II. Quinine and strychnine.** R. N. Bhattacharya and A. K. Ganguly (*J. Pharm. Pharmacol.*, 1954, **6** [3], 191–194).—Values of $E^{1\%}_{1\,cm}$ at 231, 252, 270, 317 and 347 mμ of quinine (**I**) in 0·1 *N* HCl are 319·4, 825·2, 21·12, 131·3 and 164·1, respectively; the corresponding values for strychnine (**II**) are 116·3, 355·2, 178·3, 0 and 0. For the determination of **II** and **I** present in mixtures in ratios from 1 : 40 to as low as 1 : 250, the soln. is suitably diluted and **I** is determined from absorption at 347 mμ. Another portion of the soln. is so diluted that the absorption at 270 mμ due to **I** alone would be ≃ 1 (solution A). From a standard stock solution of pure **I** a dil. soln. (solution B) having an absorption of ≃ 1 is prepared. The absorption of soln. B at 270 mμ is measured and the wavelength dial of the instrument is set at the point (about 385 mμ) where absorption equals that at 270 mμ. Absorption of soln. A is then measured at the last setting of the dial, and then at 270 mμ; the difference between the absorptions gives an accurate estimate of the absorption at 270 mμ due to **II**. Results by this method are within 2 per cent. of calculated values. For the assay of the alkaloids in pharmaceuticals containing other ingredients, the bases are extracted and determined as hydrochlorides.

S. C. Jolly

1340. **Rapid method for determining total alkaloids in *Rauwolfia Serpentina*.** L. Hörhammer and S. B. Rao (*Arch. Pharm., Berlin*, 1954, **287** [2], 75–76).—The powdered drug (3 g) is exhausted (Soxhlet) with 95 per cent. ethanol and the alkaloids are completely extracted from the residue obtained, after evaporating the ethanol, with about five 20-ml portions of hot water, which are separately filtered into a separating funnel. The alkaloids are extracted with four portions of 20 ml of $CHCl_3$ in presence of aq. NH_3, and the combined $CHCl_3$ extract is washed with water (10 ml), filtered, and evaporated to dryness in a tared flask. The residue is dried to constant wt. on a water-bath. The results are slightly higher than those obtained by the Indian Pharmacopoeia method.

P. S. Arup

1341. **The paper chromatographic separation of digitoxin and gitoxin (preliminary report).** C. Günzel and F. Weiss (*Z. anal. Chem.*, 1953, **140** [2], 89–92).—Digitoxin and gitoxin can be separated on paper pre-treated with silicone. The solvent mixture is chloroform - methanol - water (100 : 100 : 60). The $CHCl_3$ layer is used as the stationary phase. The R_F values vary considerably with the paper and the silicone, but clear separations can

be attained both with pure glycosides and extracts. The papers are sprayed with a mixture of 10 ml of glacial acetic acid, 3 drops of anisaldehyde and 6 drops of H_2SO_4, sp. gr. 1·8, and viewed in u.v. and day-light. P. S. STROSS

1342. **The chemical assay of benzathine penicillin.** G. Parker and L. Donegan (*J. Pharm. Pharmacol.*, 1954, **6** [3], 167–170).—A rapid iodimetric assay for benzathine penicillin (**I**) based on Alicino's method (*Brit. Abstr. C*, 1947, 19) is described. About 500 mg (*W*) of **I**, treated with 1 to 2 ml of approx. *N* NaOH, is shaken for 2 to 3 min. with sufficient water to effect solution and diluted to 500 ml with water. To each of three 5-ml aliquots, 5 ml of *N* NaOH are added, followed after ≮ 10 min. by 5 ml of 1·1 *N* HCl and 20 ml of 0·01 *N* I. After exactly 15 min. the excess of I is titrated with 0·01 *N* $Na_2S_2O_3$ (average titre = *S* ml). A blank determination is carried out by adding 20 ml of 0·01 *N* I to 4 to 6 mg of **I** suspended in 10 to 15 ml of water and immediately titrating with 0·01 *N* $Na_2S_2O_3$ (*B* ml). Potency of the sample (*P*) in i.u. per mg = $[(B-S) \times 0{\cdot}01 \times 6615]/W$ and percentage purity = $(P \times 100)/1307$. Alternatively the purity can be determined from the dibenzylethylenediamine contents, for which a method is given depending on the extraction and titration of the base. Both methods gave results in reasonable agreement with those of biological assay. S. C. JOLLY

1343. **The assay of penicillin in compound feeding stuffs.** S. A. Price and K. A. Boucher (*Analyst*, 1954, **79**, 150–158).—A large-plate method derived from the pad - plate technique of Esposito *et al.* (*Fed. Proc.*, 1952, **11**, 208) is described for the assay of penicillin in feeding stuffs. The primary standard solution is a dilution in methanol of a buffered aq. soln. of Na benzylpenicillin. Methanolic extracts of the sample are taken up on paper discs and the dried discs are applied to the medium in a randomised Latin-square assay design and incubated for 16 to 18 hr. at 30° C; the zone diameters are then measured. The limits of accuracy of the method are of the order of 90 to 111 per cent. in an 8 × 8 assay of 2 samples with 8 replicates per dose or 85 to 117 per cent. if 4 samples are accommodated in the pattern and the replicates are reduced to 4. A. O. JONES

1344. **Complexometric titration of pharmaceutical calcium compounds.** J. S. Faber (*Pharm. Weekblad.*, 1954, **89** [9–10], 129–142).—The principles underlying the complexometric titration with disodium ethylenediaminetetra-acetate are explained. Results obtained by indirect (with Eriochrome black T as indicator) and direct (with murexide) methods for the determination of Ca in Ca amygdalate, $CaCl_2$, Ca gluconate, Ca glycerophosphate, Ca lactate, Ca laevulinate, Ca pantothenate and Ca saccharate compare well with those obtained by gravimetric and volumetric oxalate methods. The complexometric methods are quicker. S. C. JOLLY

1345. **Determination and identification of allyl and thiobarbiturates in the presence of other barbiturates.** R. L. Herd (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 209–215).—Total barbiturates are determined gravimetrically (Methods of Analysis, A.O.A.C., Seventh Edition, p. 590). For the determination of alkene barbiturates, the weighed residue, dissolved in methanol and acidified, is titrated with KBr - $KBrO_3$ soln., KI is added and the soln. is titrated with $Na_2S_2O_3$. Thiobarbiturates are determined by a similar procedure in which S is oxidised to SO_4''. The other barbiturates are determined by difference. The method is not applicable to vinbarbitone, cyclobarbitone, hexobarbitone or bromoallylbarbiturates. Solubilities and m.p. are recorded. A. A. ELDRIDGE

1346. **A photometric method for the determination of Anaesthesin [benzocaine] and some other aromatic amines by the Lauth reaction.** J. Kolšek (*Z. anal. Chem.*, 1953, **140** [6], 426–429).—The reaction discovered by Lauth of primary, secondary and tertiary aromatic amines in acetic acid soln. with lead dioxide, which so far has been used only qualitatively is used for quant. estimation. Benzocaine (0·25 to 1 mg) is dissolved in 10 per cent. acetic acid (5 ml), a small quantity of PbO_2 is added and the mixture is shaken for 3 min. The red soln. formed is extracted with ether (10 ml) and the colour is measured exactly 10 min. after addition of PbO_2. Other amines give coloured compounds which are not ether-soluble and the aqueous soln. can be measured after filtration. Diphenylamine, 1-naphthylamine, *p*-toluidine, benzidine, phenylenediamine and *o*-tolidine were also determined. Amines with nitro groups attached to the benzene ring do not react. P. S. STROSS

1347. **Analysis of β-piperidinoethyl *p*-propoxyphenyl ketone (Falicain).** H. Bräuniger and H. -W. Raudonat (*Arch. Pharm., Berlin*, 1954, **287** [2], 82–90).—Characteristic derivatives (oxime, dinitrophenylhydrazone, Reinecke and diamminetetranitro - Co complexes) and their prep. are described; the absorption spectrum graph of Falicain is also given. As the compound consists in the hydrochloride, the Cl′ may be determined directly by the Volhard method, or (more accurately) on the thiocyanate - Reinecke complex obtained by Hannig's and Vogt's procedures (*cf. Pharmazie*, 1953, **8**, 28, and *Pharm. Zentralh.*, 1951, **90**, 2). Propoxyl may be determined by the Zeisel method (Viebock and Swappach modification), provided that the sample is refluxed for 1 hr. at 140° C with the aq. HI (and 0·2 g of red P) before distillation of the propyl iodide. Directions are given for the colorimetric determination (with tabulated results for various concn.) of Falicain through the Reinecke complex in acetone soln., through the above Co complex, or by the coloration produced with *m*-dinitrobenzene in alkaline ethanolic soln. P. S. ARUP

1348. **The estimation of *p*-aminosalicylic acid.** G. K. Rao, R. Natarajan, K. R. K. Rao and J. N. Tayal (*J. Pharm. Pharmacol.*, 1954, **6** [3], 195–198).—Results obtained by bromination, diazotisation and spectrophotometric methods of assay for *p*-aminosalicylic acid (**I**) and its salts have been compared with a new method involving decarboxylation followed by diazotisation. In this new method about 0·5 g of **I** is heated gently under a reflux condenser with 100 ml of *N* H_2SO_4 under slight suction and the liberated CO_2 is drawn out of the reaction flask with a stream of CO_2-free air through a series of 3 absorption bulbs attached to the top of the reflux condenser, each containing 50 ml of 0·2 *N* $Ba(OH)_2$ containing 2 per cent. of $BaCl_2$. Heat and suction are increased, and after 2 hr. the excess of 0·2 *N* $Ba(OH)_2$ is titrated with HCl and phenolphthalein; a blank determination is carried out. Each ml of 0·2 *N* $Ba(OH)_2 \equiv 0{\cdot}01531$ g of **I**.

The soln. remaining in the reaction flask is diluted to 250 ml, and, to a 100-ml aliquot, 10 ml of HCl are added; the soln. is cooled below 15° C and titrated against 0·1 *M* $NaNO_2$ with starch - KI paste as external indicator; each ml of 0·1 *M* $NaNO_2$ ≡ 0·0153 g of **I**. With pure substances, assay values of 98 to 102 per cent. are obtained with the diazotisation process when those with the decarboxylation process are ≮ 98 per cent.; if the decarboxylation process gives low results those by diazotisation are abnormally high, indicating excessive amounts of *m*-aminophenol (**II**). The accuracy of the assay can be checked by determining the m.p. of **II** extracted from the 150 ml of soln. remaining; any variation from 121° to 123° C indicates the presence of isomers of **I**. The new method is lengthy, but the results are more uniform than those given by existing methods. S. C. JOLLY

1349. **Estimation of isoniazid.** E. I. Short (*Lancet*, 1954, **i** [13], 656–657).—The method depends on the reaction of the $\cdot NH_2$ group of the hydrazide fraction of the molecule with 1:2-naphthaquinone-4-sulphonic acid. To the protein-free filtrate of plasma or serum (9 ml) is added 1 ml of 0·1 per cent. w/v sodium 1:2-naphthaquinone-4-sulphonate soln. and the colour is allowed to develop in the dark for 1 hr. The colour (max. at 455 mμ) is measured absorptiometrically in 4-cm cells, the readings being made against a similarly treated blank filtrate through an Ilford No. 601 or 621 filter. The isoniazid level is determined from a standard curve. Procedures are given for blood, tissues and urine. Results in the range 0·125 to 0·6 mg per 100 ml of serum range from 90·0 to 112·8 per cent. of theory with a mean standard error varying from ± 2·6 to ± 3·7 per cent. at different levels. N. E.

1350. **Method of estimating isoniazid in biological fluids.** W. F. J. Cuthbertson, D. M. Ireland, W. Wolff and S. W. A. Kuper (*Brit. Med. J.*, 1954, **i**, 609–611).—Plasma from heparinised blood is deproteinised with Na tungstate and H_2SO_4 at 100° C. The soln. is neutralised and buffered, and isoniazid is extracted into *n*-butanol - ether (1 + 3 v/v) mixture and then into 0·1 *N* HCl. The HCl extract is neutralised and buffered, freshly prepared picryl chloride soln. is added, and the soln. is heated at 100° C for 20 min. After addition of 5 *N* acetic acid, the coloured product is extracted with *n*-butanol and determined absorptiometrically with the aid of a blue-green filter. Isoniazid in urine is determined similarly, but without protein pptn. Standard samples must be tested concurrently. The method cannot be used in the presence of *p*-aminosalicylic acid, but streptomycin, *iso*nicotinic acid, *iso*nicotinoylglycine or an unidentified metabolite of isoniazid present in urine do not interfere. C. E. SEARLE

1351. **A note on the titration of sulphonamides in non-aqueous solvents.** J. S. Faber (*J. Pharm., Pharmacol.*, 1954, **6** [3], 187–190).—Titration of 0·5 g of sulphonamide, suspended in 40 ml of benzene - methanol mixture (3 + 1) or dissolved in 50 ml of pyridine, against 0·1 to 0·2 *N* Na methoxide (standardised against 0·25 g of benzoic acid) with 0·2 ml of thymol blue soln. (0·1 g in 100 ml of methanol) as indicator gives results agreeing well with those obtained by the official nitrite titration methods. The method is applicable to sulphathiazole, sulphadiazine, sulphamerazine, sulphadimidine and succinylsulphathiazole, but not to sulphanilamide. For the assay of tablets, pyridine is the better solvent; some excipients interfere. S. C. JOLLY

1352. **Experimental investigation into testing the disintegration rate of tablets with a new apparatus.** H. Braun and H. Huber (*Dtsch. Apoth.Ztg.*, 1954, **94** [8], 149–152).—Methods available for determining the disintegration times and standards of tablets from various countries are discussed. A new apparatus and procedure are described, in which the tablets are placed in a rotating wire cage. The results obtained on a number of tablets are recorded. Tablets of Ca salts had considerably longer disintegration times than had the other tablets examined. S. C. JOLLY

1353. **The chemical composition of certain grades of Puerto Rican tobacco, type 46.** M. Phillips, F. B. Wilkinson and A. M. Bacot (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1157–1165).—Results of determinations of sand, water-sol. and water-insol. ash, alkalinity of ash, Cl, light-petroleum extractives, N, nitrate N, ammonia N, protein, nicotine, total reducing substances, pectin extracted with acid, pectic acid and pectates, pentosans, cellulose, lignin, oxalic acid, citric acid and *l*-malic acid are tabulated. A. A. ELDRIDGE

See also Abstract 1401.

Food

1354. **Determination of moisture in foods by hydrogen nuclei magnetic resonance.** T. M. Shaw, R. H. Elsken and C. H. Kunsman (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1070–1076).—The determination of water by measurement of the nuclear magnetic absorption of hydrogen nuclei (Shaw and Elsken, *Brit. Abstr. AI*, 1950, 775), can be applied to foods. For starch and pectin the useful range is 7 to 20 per cent. with an accuracy of about ± 0·2 per cent. The precision depends on the reproducibility of the packing of the test specimens, and is lower for materials consisting in large particles. A. A. ELDRIDGE

1355. **Determination of lead in foodstuffs.** H. C. Lockwood (*Analyst*, 1954, **79**, 143–146).—A method for determination of Pb in foodstuffs based on extraction of the dissolved ash with diethylammonium diethyldithiocarbamate (**I**) at pH 7 is described. The material is charred with $Ca(NO_3)_2$, ignition of the fumes being avoided. The HCl extract of the ash is adjusted to pH 7 with a citrate - acetate buffer and then is extracted with a solution of **I** in CCl_4. The complex, after removal of solvent, is decomposed with H_2SO_4 and $HClO_4$ and, after suitable additions of the buffer solution, aq. NH_3 and KCN, is titrated in a separating funnel with a standard dithizone solution in $CHCl_3$, the red $CHCl_3$ layer being removed after each 1 ml addition of titrant until the final addition separates as a green or blue layer. The pH of the aq. layer is maintained at 8 to 9 during the titration by addition of aq. NH_3 and testing with universal indicator paper. Bi interferes but it can be detected by extraction of the $CHCl_3$ extract with 1 per cent. HNO_3 and addition of urea. A. O. JONES

1356. **A note on a bomb technique for preparing samples for determination of lead in foodstuffs.** D. A. Elvidge and D. C. Garratt (*Analyst*, 1954, **79**,

146–147).—In order to avoid possible loss of metal in dry ashing procedures and the high blank values of wet ashing processes, combustion was carried out in a closed vessel in an atm. of O. The Mahler - Cook bomb proved suitable for this purpose. The amount of material that can be burnt is limited by the size of the silica crucible and the max. pressure that may safely develop inside the bomb. Under an initial pressure of 30 atm., 3 to 4 g of material can be safely burnt; larger amounts necessitate several combustions. Allowance must be made for any metal contributed by the igniting fuse wire. After combustion and release of pressure from the cooled bomb the crucible and the aq. washings of the interior of the bomb are treated with dil. HNO_3 and the Pb is determined by any suitable method.

A. O. JONES

1357. **Some applications of radiography to the examination of foods and drugs.** J. F. Nicholson (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 148–153).—Defects in grains of maize and rice can be detected by means of X-rays. Radiographs of cardamom, coriander, mollé, allspice, coffee, maize, rice and beans are reproduced. A. A. ELDRIDGE

1358. **The law of Lambert - Beer, and colour determination in raw cane sugars after Celite filtration.** F. W. Zerban and L. Sattler (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1093–1095).—Beer's law holds within the limit of transmittancy measurements for solutions obtained when Celite analytical filter aid is used as previously reported (*J. Ass. Off. Agric. Chem.*, in the press). A. A. ELDRIDGE

1359. **[Analysis and] carbohydrate composition of "Hydrol."** E. M. Montgomery and F. B. Weakley (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1096–1108).—"Hydrol" (the final mother liquor remaining after separation of crystalline sugar from refined corn-sugar syrup) contains $\simeq$ 65 per cent. of saccharides; chromatographic analysis was confirmed by the anthrone method. The reducing power, expressed as dextrose, accounts for $\simeq$ 85 per cent. of the carbohydrates present. 6-[α-D-Glucopyranosyl]-D-glucose, gentiobiose, 4-[α-D-glucopyranosyl]-D-glucose and α-D-glucopyranosyl-α-D-glucopyranoside were identified.

A. A. ELDRIDGE

1360. **Some collaborative investigations of methods for isolating extraneous material from white flour.** E. J. Kiteley (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 139–147).—The following methods for isolating extraneous material from white flour are compared: (*i*) pancreatin digestion—petrol flotation, (*ii*) HCl digestion—petrol flotation and (*iii*) HCl digestion—mineral-oil flotation. Method (*i*) gave the highest recovery of insect fragments, and method (*iii*) that of rodent hairs. A 1-litre Squibb separating funnel gave higher recoveries than a 2-litre Wildman trap flask. During stirring undue turbulence should be avoided. A. A. ELDRIDGE

1361. **Recent advances in extraction technique [for separating insect and rodent filth].** M. G. Yakowitz (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 137–139).—For certain foods the use of the surface-active agent Tween 80 and a chelating agent, Versene (tetrasodium ethylenediaminetetra-acetate) in petrol - 60 per cent. ethanol in flotation procedures is recommended; the Versene reagent is hygroscopic, and the mixture should be prepared quickly. For the enzymic digestion method pancreatin is still preferred, and the boiling procedure should be avoided. A. A. ELDRIDGE

1362. **An approach to insect larval identification by structures isolated as fragments from cereal products.** O. L. Kurtz (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 167–169).—A brief review, with diagrams of characteristic structures.

A. A. ELDRIDGE

1363. **Rapid automatic estimation of water and ash in flours.** C. Duval (*Chim. Anal.*, 1954, **36** [3], 61–62).—By means of a self-recording thermobalance, the contents of absorbed H_2O, combined H_2O (with N), and ash in flour can be estimated reasonably accurately within 3 hr. by heating a 300-mg sample to $\simeq$ 820° C at a uniform rate of 300° per hr. The calculated values from the graph of wt. loss plotted against temp. for absorbed H_2O are within 0·01 per cent. of those obtained by the Karl Fischer method. The 110° isotherm for any kind of flour may also be obtained.

W. J. BAKER

1364. **Revision of P. Antón's bran-tables, and anomalies that occur in bread-flours.** A. Quintana Mari and M. Garcia Garvia (*An. Bromatologia*, 1953, **5** [1], 99–118).—To facilitate the estimation of the degree of extraction of flour, without regard to the type of wheat from which it was derived, and to obtain a more reliable figure than that based on the ash content, P. Antón (*Hojas Divulg. Centre. Cereal.*, 1939, No. 9) established a table relating extraction to the quantity of dried bran collected on a No. 120 sieve during the washing of gluten. Sieving test results are influenced by the fineness of the bran and Antón published two tables, one for normal flour, and the other for remilled flour. An investigation showed that (*i*) the table of P. Antón could not be used with flour from very hard wheats or with heavily milled flour, (*ii*) flour from Spanish wheats between 78 and 94 per cent. extraction showed a slight inflection in the curve and (*iii*) for flours of lower extraction, a considerable departure from Antón's table was observed which might be the result of the lower weight per hectolitre (bushel weight) of Spanish commercial wheats. H. PRITCHARD

1365. **The use of anthrone for the quantitative estimation of lactose in dairy products.** H. J. Fagen, E. Sibbach and R. V. Hussong (*J. Dairy Sci.*, 1954, **37** [1], 10).—Quant. determination of lactose in milk and cheese by means of Dreywood's anthrone reagent (*Brit. Abstr. C*, 1946, 280) has been shown to give results in good agreement with copper-reduction methods. *Procedure*—To 2·5 ml of the solution containing 10 to 50 μg of lactose in a 50-ml Erlenmeyer flask cooled in ice, add 10 ml of anthrone reagent (dissolve 1 g of anthrone in 50 ml of H_2O, cool in ice and slowly add conc. H_2SO_4 to 500 ml). Place in a bath of boiling water for 5 min., and immediately read the colour through a Lumetron 580 filter. Read off the lactose content from a standard graph prepared by treating similarly known soln. of lactose. The high dilution prevents interferences from fats and protein.

D. C. M. ADAMSON

1366. **The identification of dung and plant fragments in dairy products.** D. B. Scott (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 177–181).—Technique for staining with ruthenium red is

described and discussed. Cell walls containing some pectic substances and some nutritive elements, but not mucilage on the surface of dung fragments, are stained pink. A. A. ELDRIDGE

1367. **Rapid determination of water-insoluble fatty acids in cream and butter.** F. Hillig (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1077–1083).—The fat is separated in granular form by shaking cream with water at 10° C; butter is first melted and then cooled to a creamy consistency before shaking with water. The butter obtained is washed well with water, dissolved in ether, and titrated with Na ethoxide (1 ml of 0·05 *N* Na ethoxide ≡ 13·5 mg of fatty acids). A. A. ELDRIDGE

1368. **Chromatographic determination of amino-acids in cheese.** C. Petronici (*Chim. e Ind.*, 1954, **36** [1], 16–19).—The amino-acids and cations in a soln. of cheese prepared by the Söncke - Mogensen method are fixed on Zeo-carb 215 and then eluted, after washing, by *N* aq. NH_3, and the resulting soln. is chromatographed on paper by means of a solvent such as *n*-butanol, acetic acid and water (40:10:50). Identification is effected with ninhydrin and other reagents specific for individual acids; quant. determinations are made by extraction of individual colorations with ethanol and spectrophotometry of the resulting solutions. Aspartic and glutamic acids, lysine, alanine, glycine, tyrosine, tryptophan, leucine, serine, phenylalanine, valine, threonine and proline are determined.
R. C. MURRAY

1369. **Comparison of results of analyses of phosphorus in fruit spreads by official volumetric and rapid colorimetric procedures.** J. E. Despaul and C. H. Coleman (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1088–1093).—In the procedure described the molybdenum-blue reaction is used with 1-amino-2-naphthol-4-sulphonic acid at 37° C as reducing agent, the sample being ashed first. The average deviation (mg of P_2O_5 per 100 g) was 1·7 for jam and 1·5 for jelly; plum and grape jam give negative deviations only, being respectively 1·12 and 0·925. A. A. ELDRIDGE

1370. **Comparison of results of analyses for potassium in jam and jelly by the chloroplatinate and flame-photometer methods.** J. E. Despaul, H. B. Weissman and M. H. Barsky (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1083–1087).—For the flame photometer method ashing is unnecessary; a dil. soln. of the sample is atomised through the instrument, the determination occupying 10 min. The estimated standard deviation per 100 g is ± 3·36 mg of K_2O; that of the chloroplatinate method is ± 1·01 mg of K_2O. Borderline or deficient quantities indicated by the flame photometer method should be confirmed by the official (A.O.A.C.) method. A. A. ELDRIDGE

1371. **The determination of the carotenoid content of tomatoes, its relation to degree of ripeness and its application to analytical control of tomato extracts.** J. C. Sanahuja (*An. Bromatologia*, 1953, **5** [3], 245–253).—The work of F. G. Stock (*Brit. Abstr. C*, 1950, 340) has been applied to tomato products in Spain. The method of test was that of F. Zscheile and J. W. Porter (*Brit. Abstr. C*, 1947, 83). In mature tomatoes the lycopene content is almost constant at 1000 μg per g of dry extract. Figures are given for samples containing various amounts of green tomatoes. H. PRITCHARD

1372. **Mould and rot in tomato ketchup.** T. H. McCormack (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 162–167).—Microscopical diagnostic characters are described and illustrated. The Howard mould count method is appropriate. Rot fragments are detected by staining with gentian violet.
A. A. ELDRIDGE

1373. **Analysis of Sicilian lemon oils.** J. W. Sale (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1188–1189).—Values are recorded as follows: base line absorption (line CD) 0·68 to 0·73, total absorption at peak (≃ 315 mμ) 1·24 to 1·37, steam-distillation residue 2·55 to 3·35 per cent. A. A. ELDRIDGE

1374. **Flame spectrum of whisky. Determination of sodium and potassium.** M. J. Pro and A. D. Etienne (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1150–1157).—Procedure for the determination of Na and K by means of a Beckman DU spectrophotometer with flame photometry attachment and an oxygen - hydrogen flame is described; readings were taken at 570, 589 and 610 mμ for Na and at 740, 768 and 790 mμ for K. The straight whiskies contained ⩾ 10 p.p.m. of Na and ⩾ 35 p.p.m. of K. Traces of Ca were detected.
A. A. ELDRIDGE

1375. **Apparatus for determination of volatile acidity and alcoholic content of wines.** G. Cesaire and R. Rougieux (*Chim. Anal.*, 1954, **36** [3], 70–73).—An all-glass apparatus effects water-vapour entrainment of volatile compounds in wines by means of a small deep glass bulb designed to admit water vapour from a 600-ml distillation flask inside which it is fitted and connected, through the neck, to a three-bulb reflux column, condenser and receiving flask. In the estimation of volatile acidity, ≃ 1 to 2 ml of wine (freed from CO_2 and containing an added small amount of tartaric acid) are placed in the deep bulb partly immersed in gas-freed distilled water in the large flask, and steam-distillation is continued for ≃ 25 min. until ≃ 30 ml of distillate are collected; entrainment of lactic acid is negligible. For the estimation of alcoholic content, 150 ml of wine neutralised with 5 *N* NaOH and diluted to 250 ml with pure water are slowly distilled from the large flask until the vol. of distillate is approx. 80 per cent. that of the original wine; the small bulb and the reflux bulbs prevent entrainment of impurities. Values obtained for both estimations are in excellent agreement with those obtained by standard distillation techniques. W. J. BAKER

1376. **Extraneous materials in spices.** T. H. McCormack (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 157–161).—Types of contaminants found in spices by flotation, sedimentation and macroscopic examination are listed. The cigarette beetle, confused flour beetle, saw-toothed grain-beetle and Indian meal moth (all illustrated) are frequently found. A. A. ELDRIDGE

1377. **The microbiological determination of thiamine. Report by the Thiamine (Microbiological) Panel of the Sub-Committee on Vitamin Estimations of the Analytial Methods Committee of The Society for Analytical Chemistry.** (*Analyst*, 1954, **79**, 118–121).—After reviewing existing methods for the microbiological determination of thiamine the Panel has concluded that two methods are likely to yield results of acceptable accuracy with a reasonable range of foodstuffs when applied by

analysts with no practical experience of the assay. These are the plate method of Jones *et al.* (*Brit. Abstr. C*, 1949, 409) and the tube method of Fitzgerald *et al.* (*Brit. Abstr. C*, 1949, 409), the test organism in each being *Lactobacillus fermenti* **36**. These methods have been subjected to collaborative work and, with the modifications suggested, are recommended as having the required accuracy.

A. O. JONES

1378. **Microbiological procedure for the assay of pantothenic acid in foods: results compared with those by bioassay.** E. W. Toepfer, E. G. Zook and L. R. Richardson (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 182–190).—Procedure for the microbiological determination of total pantothenic acid in foods by use of intestinal phosphatase and liver enzymes for preparation of sample extracts is described. Results were higher than those obtained by the Mylase-P method. For the samples examined the results were in good agreement with those resulting from rat bioassays.

A. A. ELDRIDGE

1379. **The separation and identification of L-ascorbic, D-*iso*ascorbic and D-glucoascorbic acids by paper chromatography.** L. C. Mitchell and W. I. Patterson (*J. Ass. Off., Agric. Chem.*, 1953, **36** [4], 1127–1130).—Paper is impregnated with 1 per cent. aq. HPO_3 and dried before spotting. The mobile solvent is a mixture of acetonitrile, acetone, water and glacial acetic acid (80:5:15:1), and ammoniacal $AgNO_3$ soln. is used as indicator.

A. A. ELDRIDGE

1380. **A white mutant of the green alga *Euglena gracilis var. bacillaris* suitable for the microbiological determination of the B_{12}-vitamins.** H. L. C. Heinrich, H. Hill and S. Brilling (*Naturwissenschaften*, 1953, **40**, 144–145).—A white mutant of *Euglena gracilis* var. *bacillaris* was accidentally discovered in residues containing oxytetracycline (Terramycin) from an antibiotic fermentation. This mutant is unable to undergo division in absence of vitamin B_{12}, but is stimulated into active growth on addition of a few millimicrograms of crystalline vitamin B_{12}; the limiting concn. being 10^{-12} g of B_{12} per ml, and the 7-day incubation period required by the green form can be reduced to 3 or 4 days.

P. HAAS

See also Abstracts 1333, 1334.

Sanitation

1381. **Dissolved-oxygen measurement.** A. T. Ippen and C. E. Carver, jun. (*Instruments and Automation*, 1954, **27** [1], 128–129).—Continuous measurement of dissolved-oxygen concentrations is possible with either the dropping-mercury electrode or the rotating-platinum electrode. Construction and use of the two electrodes are detailed. Results obtained by the dropping-mercury electrode under conditions of minimum turbulence agree well with those by the Winkler method. The rotating platinum electrode is less affected by turbulence, since its operating principle depends on extensive mixing close to the platinum wire, but the necessity of keeping its wire tip polished probably restricts its use to clear waters.

D. R. GLASSON

1382. **Rapid micro-colorimetric determination of dissolved oxygen.** W. F. Loomis (*Anal. Chem.*, 1954, **26** [2], 402–404).—A colorimetric method for determining dissolved O in 0·5-ml samples is described. It takes about 1 min. The colour change from yellow to red that occurs when a soln. of reduced indigo carmine is partly oxidised by the O in the test sample is measured. No specialised equipment need be constructed, as a standard tuberculin syringe is adapted for direct use in the absorption cell of a Beckman DU spectrophotometer, which can detect changes in concn. as small as ± 0·2 mg of O per litre over a range extending from fully anaerobic to fully aerobic conditions. A calibration curve showing the essentially linear relationship of absorbance at 580 mμ to percentage saturation with air is presented and its construction is described. The slight change in "blank" absorbance between reduced and oxidised samples introduces an error of less than 1 per cent. Compounds capable of oxidising or reducing indigo carmine, such as nitrates, chlorates, nitrites, iron salts and sulphites, interfere with the method unless previously removed.

O. M. WHITTON

1383. **Studies in ozonisation. I. The estimation of ozone.** A. E. Rawson (*Wat. & Wat. Eng.*, 1953, **57**, 56–64).—Results are given of experiments on the determination of ozone in air and in solution. It is concluded that colorimetric methods by acidified *o*-tolidine are not reliable. Addition of excess of potassium iodide and titration with sodium thiosulphate in presence of a strong acid such as H_2SO_4 is accurate. Ferrous ammonium sulphate or sodium arsenite can also be used for the volumetric determination of ozone. In an accurate colorimetric method involving the blue starch - iodine colour, neutral potassium iodide is added to the test solution, which is then acidified with sulphuric acid. Five min. after addition of starch the colour is matched against 0·005 or 0·001 *N* $KMnO_4$ or I soln. that has been similarly treated. Concentrations of ozone in solution up to 5·0 p.p.m. have been studied and reliable results have been obtained. Detailed procedures for the methods tested are given in an appendix.

WATER POLLUTION ABSTR.

1384. **Determination of calcium and magnesium in lake waters by means of a rotating silver-disc electrode.** V. W. Meloche and R. Shapiro (*Anal. Chem.*, 1954, **26** [2], 347–350).—A rapid sensitive spectrographic method was developed for determining Ca and Mg in lake waters. A silver disc electrode, fabricated by the method given, was used. The range of concn. studied was 0·1 to 30 p.p.m. Before re-use, the electrodes were rinsed in conc. HCl to remove the oxide coat and residues from previous analyses. The standard deviation of a single measurement, based upon 4 observations on a given sample, was found to depend on the spectral line pair employed and on the concn. The sensitivity and reliability of the method in the range of 0·1 to 1 p.p.m. are somewhat superior to those of the flame-photometric method.

O. M. WHITTON

1385. **The precise and routine potentiometric determination of the chlorinity of sea water.** J. M. Bather and J. P. Riley (*J. Cons. Int. Explor. Mer*, 1954, **18**, 277–286).—A potentiometric method for determining the chlorinity of sea water is described. A 15-ml sample of sea water is weighed and diluted with 20 ml of distilled water. A magic-eye valve voltmeter is used to indicate the end-point and is set, by means of a potentiometer, at 0·135 V, the potential of a platinum electrode at the end-point during titration of chloride with $AgNO_3$. Aq.

$AgNO_3$ (0·2173 *N*) is added until the magic eye begins to close, then a more dilute $AgNO_3$ soln. (0·004346 *N*) is added until the shadow lines become parallel at the end-point. Determinations made with sea water of standard strength have shown that the standard deviation is of the order of 0·005 per cent. The method should not be applied to samples having a pH value of less than 6·5. A diagram is given of the electrical circuit.

WATER POLLUTION ABSTR.

1386. **The use of paper chromatography in the estimation of aluminium in mineral waters.** K.-E. Quentin (*Z. anal. Chem.*, 1953, **140** [2], 92–102).—HCl is added to the sample and the soln. is concentrated to small vol. in a platinum dish. NH_4Cl and 1 mg of Fe^{III} are added and the soln. is made ammoniacal. The ppt. is filtered hot, dissolved in dilute HCl and spotted on paper. The solvent for the ascending chromatography is a mixture of acetone (45 per cent.), ethyl acetate (45 per cent.), water (5 per cent.) and HCl, sp. gr. 1·19, (5 per cent.). The paper is then either sprayed with aluminon (100 mg of aluminon in 100 ml of acetate buffer at pH 4·2) and exposed to ammonia vapour or sprayed with a saturated alcoholic soln. of morin. The Al spots (R_F = 0) are compared with standards. For accurate determinations, Al is eluted and determined colorimetrically with aluminon at pH 4·2. As little as 0·01 μg can be detected with morin.

P. S. STROSS

1387. **New colorimetric micro-determination of vanadium in natural waters.** K. Sugawara, M. Tanaka, and H. Naitô (*Bull. Chem. Soc. Japan*, 1953, **26** [8], 417–420).—The water sample (5 to 20 litres) is acidified with HCl, $Fe(NO_3)_3$ is added until the Fe concn. is 10 mg per litre and then 1 ml of *M* NaOCl is added for each litre of soln.; the mixture is warmed on a water-bath and neutralised with 2 *N* aq. NH_3 to bromothymol blue or bromocresol purple and then filtered. The pH is then the optimum for the co-precipitation of V with $Fe(OH)_3$. The paper and ppt. are ignited, and the ash is ground with Na_2CO_3 (3 g) and fused (40 to 60 min. in a platinum crucible). After the residue has been transferred with hot water to a beaker and digested with 2 to 5 drops of H_2O_2 (to ppt. Mn) and 30 to 40 ml of water, the extract is filtered. The extract is neutralised to *p*-nitrophenol by warming and adding H_2SO_4, 2·5 ml of 4 *N* H_2SO_4, 1 ml of 5 per cent. malonic acid soln. (to mask Al) and 0·5 ml of 2 per cent. oxine soln. are successively added, and the mixture is transferred to a separator, buffered with 4 ml of 4 *N* Na acetate and extracted twice with $CHCl_3$ (3 ml and 2 ml). Then 0·2 ml of 2 per cent. oxine soln. is added and the soln. is further extracted with $CHCl_3$. The combined $CHCl_3$ extract is evaporated on a water-bath in a platinum crucible with 1 g of Na_2CO_3 and ignited; the product is digested with H_2O, filtered and neutralised to *p*-nitrophenol, 1 ml of *N* H_2SO_4 is added and the soln. is boiled and cooled. The soln. is made up to 70 to 100 ml, 0·5 ml of oxine soln. and 6 ml of 2 *N* aq. NH_3 are added (stirring and dilution prevent pptn.) and the product is extracted with benzene to remove Fe oxinate. The extracted layer is adjusted to pH 4 with 4 ml of Na acetate soln. and 4·5 ml of 4 *N* H_2SO_4, 0·2 ml of oxine soln. is added and the V oxinate is extracted with pure pentanol. The combined extract is made up to 10 ml and the optical density is determined in a spectrophotometer at 475 mμ. The method is applicable to silicate materials and experimental work is quoted supporting the conditions specified in the above method.

F. R. MUMFORD

1388. **Detection and determination of traces of polynuclear hydrocarbons in industrial effluents and sewage. II. Sewage humus and treated effluents.** P. Wedgwood and R. L. Cooper (*Analyst*, 1954, **79**, 163–169).—The method previously described (*Brit. Abstr. C*, 1953, 322) for detection of micro amounts of polynuclear hydrocarbons in complex substances has been applied to the examination of "humus" and filtered final sewage effluents from certain sewage works. These compounds have been found whether or not industrial effluents are discharged in both activated sludge and bacterial filter-bed sewage. Gas works effluents can be a source of aromatic compounds and washings from tarred roads as well as rain and snow contribute. The amount of hydrocarbon in humus or final effluent appear higher when biochemical oxidation is not efficient. The hydrocarbons found in humus and final effluent are listed with their absorption graphs. Complex hydrocarbons have not been found in human urine and faeces and sources other than domestic sewage are indicated.

A. O. JONES

See also Abstracts 1224, 1249, 1410.

Agriculture and Plant Biochemistry

1389. **Spectrographic analysis of minor elements extracted from plants and soils as dithizonates.** W. J. Wark (*Anal. Chem.*, 1954, **26** [1], 203–205).—Representative samples of soil (1 g) or plant ash (from 10 g of dried tissue) are dissolved by Na_2CO_3 fusion, the melt being extracted with 150 ml of water. Excess of Na citrate is added and the pH is adjusted to 8·3 with aq. NH_3. Co^{++}, Cu^{++}, Zn^{++}, Pb^{++}, Ag^{+}, Sn^{++} and Fe^{++} are extracted with successive 10-ml portions of 0·1 per cent. dithizone in $CHCl_3$. The $CHCl_3$ extract is evaporated to dryness and the residue is dissolved in 2 ml of solvent, which is evaporated again to dryness in presence of 100 mg of graphite. After ignition at 450° C, the graphite is mixed with 10 mg of Li_2CO_3 (Li is internal standard) and the elements are determined spectrographically in a cratered graphite electrode, comparison being made with standards. Determined standard deviations are: Co, ± 5 per cent.; Zn, ± 9·2 per cent.; Cu, ± 15 per cent.

D. A. PANTONY

1390. **Methods for spectrochemical trace analysis. II. Trace analysis of plant materials.** F. A. Pohl (*Z. anal. Chem.*, 1953, **139** [6], 423–429).—Major constituents must be separated before trace analysis is possible. The dried plant material is ashed at 450° to 500° C. Sulphuric acid is added and the SiO_2 is volatilised with HF. If spectrographs with small dispersion are used iron must be removed. A lengthy method to achieve this is described in detail. It is based on extraction of iron (with other elements) with HCl-saturated ether and re-extraction with ammonium thiocyanate, after reduction of iron with sodium dithionate. Trace elements are concentrated by extraction with a mixture of diethyldithiocarbamate, 8-hydroxyquinoline and dithizone in chloroform at pH 3, 5, 7 and 9. Twenty trace elements present in amounts from 0·1 μg per g of dry material can thus be determined.

P. S. STROSS

1391. **The determination of silica in biological products by emission spectroscopy.** G. A. Monnot (*Spectrochim. Acta*, 1954, **6** [2], 158–160).—Silica is determined spectrographically, a Si-free Al or Cu counter electrode being used as an external standard. Biological fluids are absorbed on a 1·5 cm sq. piece of ashless filter-paper, which is placed in the crater after being partly dried; a standard soln. of sodium silicate is used in the same way. The minimum amount of SiO_2 that can be detected is 0·3 μg and the determination can be carried out on from 10 to 1000 μg of SiO_2. E. HAYES

1392. **Boron determination in soils and plants. Simplified curcumin procedure.** W. T. Dible, Emil Truog and K. C. Berger (*Anal. Chem.*, 1954, **26** [2], 418–421).—Methods are given for the estimation of available and total B in soil and total B in plant tissue, by use of curcumin, to produce the rose-coloured rosocyanine. After prep. of an aq. soln. of the test sample, only one evaporation and one filtration are required. Comparison with the quinalizarin procedure shows good agreement. J. DAVIS

1393. **Detection of sugars and polysaccharides by a spot reaction on silk.** M. Geldmacher-Mallinckrodt (*Biochem. Z.*, 1953, **324**, 186–194).—A method is described for the characterisation of several carbohydrates by means of only 20 to 40 μg of material. Various carbohydrates can also be detected to a lower limit of 5 to 0·1 μg. A 0·002-ml drop of a 2 per cent. soln. of the carbohydrate is placed on a piece of free-hanging silk and dried in warm air. Reagents are then sprayed on to the silk and after drying the colour reaction is noted. G. W. CAMBRIDGE

1394. **New colour reactions of sedoheptulosan and its determination in mixtures of ribose and fructose.** L. Ujejski and E. R. Waygood (*Canad. J. Chem.*, 1954, **32** [1], 14–18).—Sedoheptulosan can be quant. determined in pure soln. by its colour reaction with a carbazole - H_2SO_4 reagent, or in the presence of ribose and fructose with a cysteine hydrochloride - H_2SO_4 reagent. By a combination of the two reagents, fructose can be quant. determined in the presence of the other two sugars. These reactions are not altered by hydration and may form a basis for the determination of naturally occurring sedoheptulose. N. M. WALLER

1395. **The estimation of small amounts of formaldehyde liberated during the oxidation of carbohydrates and other substances with periodate.** J. F. O'Dea and R. A. Gibbons (*Biochem. J.*, 1953, **55** [4], 580–586).—A micro-method is described for the estimation, *in situ*, of the formaldehyde arising from the oxidation of some carbohydrates and other substances with $NaIO_4$. Lead dithionate is used to remove the excess of IO_4' and inorganic reaction products. The method is applied to the products of oxidation of some monosaccharides, polyhydric alcohols, serine, and N-acetylglucosamine. The conditions under which oxidations of carbohydrates with IO_4' are most suitably performed are discussed. The determination of formaldehyde depends on the colour produced by heating with chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid) which is specific for formaldehyde. The absorption is measured at 570 mμ. B. VINEY

1396. **Analytical investigations of flavones. IV. Determination of hypericin and of hyperoside in alcoholic plant extracts.** P. Hagedorn and R. Neu (*Arch. Pharm., Berlin*, 1954, **287** [2], 70–74).—For the determination of hypericin, dark brown extracts (2 to 10 ml) are diluted (1 + 1) with water, made up with 30 per cent. ethanol to 30 ml, and extracted with 30, 10 and 10 ml of ether; after evaporation of the ether, the residue is dissolved in ethanol and made up to 25 ml. Either 2 ml of the original (lightly coloured) extract or 2 ml of the above purified extract, mixed with 1 ml of 90 per cent. ethanol and 1 ml of 10 per cent. aq. $AlCl_3$ are heated for 10 min. to 70° to 80° C, rapidly cooled, mixed with 5 ml of buffer solution (10 g of ammonium acetate and 2 ml of 30 per cent. aq. acetic acid made up with 60 per cent. ethanol to 100 ml) and made up with ethanol to 10 ml. After 30 min., the extinction value of the Al complex of the hypericin is measured at 600 to 620 mμ against a mixture of 2 ml of the extract with 0·5 ml of 30 per cent. aq. acetic acid, made up with 60 per cent. ethanol to 10 ml. For the determination of hyperoside, a mixture of the extract (1 to 2 ml diluted (1 + 9), if necessary) with 2 ml of 10 per cent. aq. $AlCl_3$ and 15 ml of the above buffer solution and made up with 60 per cent. ethanol to 25 ml is set aside for 1·5 hr. The extinction value is then measured at 430 mμ. Results for various concn. of both compounds are tabulated. P. S. ARUP

1397. **The colorimetric determination of plant succinic dehydrogenase.** E. Glock and C. O. Jensen (*J. Biol. Chem.*, 1953, **201** [1], 271–278).—A method of determining succinic dehydrogenase activity by the anaerobic reduction of *pp'*-diphenylenebis-2-(3:5-diphenyltetrazolium chloride) (**I**) is described. The coloured reduction product is extracted with *n*-butanol and shows max. absorption at 520 mμ. Standards are prepared by reducing **I** with $NaHSO_3$. The quant. of **I** reduced is linearly related to the amount of dehydrogenase. N. E.

1398. **Methods for the determination of amino-acids in sugar beets.** E. Pārnoja (*Socker Handl. I.*, 1952, **8** [7], 81–94).—The literature on chemical, chromatographic and electrophoretic methods is reviewed in detail. Beet extracts were freed from proteins and higher mol. wt. compounds by filtration several hours after precipitation with 95 per cent. ethanol. Analyses were made for soluble nitrogen, amides, NH_3 and betaine by two-dimensional paper chromatography of the amino-acids after removal of sugars (which may interfere) by McCollum's method (*Science*, 1948, **108**, 111; *Arch. Biochem. Biophys.*, 1952, **40**, 20); this method consists in evaporating the extract to dryness and dissolving the amino-acids with trichloroacetic acid in dry acetone (sugars, etc., are insol.) to form complexes which are gradually precipitated or which can be precipitated by dry NH_3 gas. The precipitate was dissolved in water and metallic ions were removed by an electrolytic de-salting apparatus before chromatographic separation. Compounds identified in the pressed beet juice were aspartic acid, glutamic acid, serine, glycine, asparagine, glutamine, α-alanine, γ-aminobutyric acid, valine, leucine, *iso*leucine and phenylalanine. Histidine, arginine and lysine were also detected (but not separated) in small amounts.

Tyrosine was not found. Electro-dialysis was also tried, but further separations were not achieved; the apparatus used is described.

SUGAR IND. ABSTR.

1399. **Evaluation of decolorising agents by colorimetry of treated solutions with light of various wavelengths.** W. Aehnelt (*Z. Zuckerind.*, 1953, **3**, 489–492).—Colorimetry of sugar solutions with the Lange colorimeter is not considered adequate if only one filter (BG5-dark blue) is used, and it is suggested that the extinction should be measured in at least three wavelength ranges (blue, red and green). The decolorising effect of some active carbons is often selective in different ways, depending upon the carbon, and upon the concentration and nuance of the initial colouring matters. Most carbons will adsorb all types of colouring matters, so that the decolorisation then depends upon the amount of carbon used, the pre-treatment of the liquors (caramel colouring matters are more difficult to remove) and the pH. Where the active carbon adsorbs both red and yellow colouring matters about equally, the residual colour may be measured as well by eye with a Duboscq colorimeter as by the extinction with a Lange colorimeter and Gibson filter. Figures and graphs are given to illustrate the possible differences. With the use of several filters, the possibility of calculating the individual differently coloured components in percentage of the total colouring matter is discussed.

SUGAR IND. ABSTR.

1400. **Properties and determination of gossypol.** C. L. Hoffpauir and W. A. Pons, jun. (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1108–1118).—The properties of gossypol are reviewed. Preliminary experiments indicate that free gossypol in mixed feeds can be determined colorimetrically after extraction with aq. acetone and reaction with *p*-anisidine (Pons and Guthrie, *J. Amer. Oil Chem. Soc.*, 1949, **26**, 671), bound gossypol requiring preliminary hydrolysis with oxalic acid in aq. ethyl methyl ketone. A. A. ELDRIDGE

1401. **Micrographic and chromatographic tests relating to the detection of ergot in rye and in some parasitic cereal plants.** S. Stoll and Y. Bouteville (*Chim. Anal.*, 1954, **36** [2], 33–37).—Ergot is separated from powdered plant materials by a gravitational method. Treatment of the separated ergot with C_6H_6 containing 2 per cent. of HCl renders it suitable for microscopic examination. Treatment of niello, vetch and melam with warm soda removes protein and protoplasmic cell constituents, leaving a cellulose structure for examination. Ergot pigments are extracted from grain with acetone containing 1 per cent. of HCl and can be estimated by direct colour comparison. A more reliable estimation of ergot pigments may be made by paper chromatography. The mixture is eluted with ammoniacal *n*-butanol and the chromatogram is developed with $AlCl_3$; ergot gives a diffuse green band whilst niello and melam give diffuse yellow bands. C. G. TAYLOR

1402. **The detection of indol-3-ylacetic acid in cauliflower heads. Chromatographic behaviour of some indol compounds.** L. E. Weller, S. H. Wittwer and H. M. Sell (*J. Amer. Chem. Soc.*, 1954, **76** [2], 629–630).—Indol-3-ylacetic acid can be identified in cauliflower heads by chromatographic techniques; the R_F values of some related indole compounds are given. The residue from an ether extract was dissolved in ethyl acetate and extracted with 1 per cent. $NaHCO_3$ soln. until the aq. soln. remained alkaline. Combined aq. extracts were acidified with H_3PO_4 and re-extracted with ethyl acetate. This extract was examined paper chromatographically by means of a mixture of *n*-propanol, 15 *N* aq. NH_3 and H_2O (60:30:10 v/v) and the descending technique. The spray reagent consisted of *p*-dimethylaminobenzaldehyde (1 g), conc. HCl (10 ml) and ethanol (90 ml). The area corresponding to between the R_F values of 0·60 to 0·90, which contained all the coloured zones as determined by developing a centre strip, was eluted with acetone.

D. LIFF

1403. **Separation and identification of chlorinated organic pesticides by paper chromatography. IV. The components of Dilan.** L. C. Mitchell (*J. Ass. Off. Agric. Chem.*, 1954, **37** [1], 216–217).—The two components [2-nitro-1:1-bis-(*p*-chlorophenyl)-propane and 2-nitro-1:1-bis-(*p*-chlorophenyl)butane] of Dilan can be separated by paper chromatography, by means of dimethylformamide as the immobile solvent and mixed octanes as the mobile solvent. The chromogenic agent is methanolic KOH and $FeSO_4$ soln. acidified with HCl.

A. A. ELDRIDGE

1404. **The electrometric measurement of soil pH.** L. E. Davis and J. M. Rible (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1146–1150).—The pH values of 28 soils, found by the use of saturated and 1/64 saturated KCl soln. in the bridge, are tabulated; the average difference is 0·11 ± 0·08 pH units. The results for saturated KCl ranged from 5·57 to 8·05, and there was no evidence of appreciable anomalous behaviour. A. A. ELDRIDGE

1405. **The ammonium chloride - liming materials reaction.** C. J. Schollenberger and C. W. Whittaker (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1130–1146).—Tests on six limestones showed that measurement of the rate of reaction between limestone and NH_4Cl (by determining the NH_3 liberated) is a satisfactory index of the activity of the limestone in soil. The procedure is detailed. Blast furnace slags do not show the same correlation.

A. A. ELDRIDGE

1406. **A study on interferences in the analysis of zinc ethylenebisdithiocarbamate.** I. Rosenthal, R. L. Carlsen and E. L. Stanley (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1170–1183).—The substance Dithane Z–78 (a fungicide based on zinc ethylenebisdithiocarbamate) is decomposed with 85 per cent. H_3PO_4, the CS_2 liberated is freed from H_2S and SO_2 by means of Pb acetate and is collected in methanolic KOH, the K xanthate formed being titrated with I soln. Interference from substantial amounts of various inorganic contaminants is thus avoided; methods for eliminating the effect of larger amounts are proposed. The effect of various conditions on the decomposition of Zn ethylenebisdithiocarbamate is discussed. A. A. ELDRIDGE

1407. **Separation and identification of chlorinated organic pesticides by paper chromatography. III. Aldrin, Isodrin, Dieldrin and Endrin.** L. C. Mitchell (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1183–1186).—The original procedure (*Brit. Abstr. C*, 1953, 226) is modified; the mobile solvent is pyridine and water (3 + 2 v/v), and 2 *N* KOH is sprayed on both sides of the paper. All possible combinations of the four components can be separated. A. A. ELDRIDGE

1408. **Rodent and insect contamination of corn and corn meal.** K. L. Harris, J. L. Trawick, J. F. Nicholson and W. Weiss (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1037–1064).—The average ratio of insect fragments in bolted maize meal to whole insects or equivalent (heads, capsules, skins) in the corn as measured by the cracking and flotation test was 12·5:1. Correlation between insect fragment counts in degerminated products and insects in the corn is low. The incidence of insect contamination is higher for white than for yellow corn; the reverse is true for rodent pellet contamination. A. A. ELDRIDGE

1409. **Use of simple blowing device to facilitate inspection of wheat for internal infestation.** M. Milner, E. P. Farrell and R. Katz (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1065–1070).—When sieved grain is blown in a seed-testing device (Milner, *Milling Production*, 1951, Jan.), the kernels with insect-emergence holes are segregated, thus rendering their detection easy. A. A. ELDRIDGE

See also Abstracts 1295, 1296, 1297.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

1410. **Instrumentation in the laboratory.** J. H. Wyatt (*J. Amer. Wat. Wks. Ass.*, 1953, **45**, 129–144).—An account is given of laboratory instruments used in the quant. analysis of water that depend on measurements of inter-action with radiant and electrical energy. The accuracy, sensitivity and applicability of each instrument are indicated. Emission and absorption photometric methods, potentiometric and polarographic measurements, and amperometric, coulometric and conductimetric titrations are discussed.
WATER POLLUTION ABSTR.

1411. **Capillary pipettes.** British Standards Institution (B.S. 797:1954, 13 pp).—Three types of pipette are specified: (*i*) graduated pipettes calibrated for delivery from zero mark to graduation mark, of capacity 0·1, 0·2 and 0·5 ml; (*ii*) graduated pipettes calibrated for content, of capacity 0·1, 0·2 and 0·5 ml; and (*iii*) one-mark pipettes calibrated for content, of capacity 0·005, 0·01, 0·02, 0·05, 0·1 and 0·2 ml. The specifications cover the material, dimensions, jet, finish of top, graduations, tolerances on capacity and inscriptions. A procedure is given for the determination of capacity.
H. P. PAGET

1412. **Ammonia distillation apparatus (Markham).** British Standards Institution (B.S. 1428:Part B2: 1953, 6 pp).—The design and suitable dimensions are specified for a steam-jacketed distillation apparatus of the Markham type for the micro-determination of N by the Kjeldahl method when the quantity of distillant is < 25 ml. The apparatus may be in one piece or a ground-glass joint may be used to connect the distillation vessel and the condenser. H. P. PAGET

1413. **Acetyl group determination apparatus (Wiesenberger).** British Standards Institution (B.S. 1428:Part C2:1954, 6 pp).—The design and dimensions are specified for the apparatus used in the micro-determination of acetyl and C-methyl groups by the Wiesenberger method (*Mikrochem. Mikrochim. Acta*, 1947, **33**, 51). The components specified are: (*i*) reaction flask; (*ii*) still-head, incorporating a vapour-trap, funnel with long-handled stopper, and spray-trap in the outlet limb; and (*iii*) water-jacketed condenser.
H. P. PAGET

1414. **Micro-centrifuge accessories.** British Standards Institution (B.S. 1428: Part E3: 1953, 6 pp.).—The design and dimensions of the following types of micro-centrifuge tube are specified: (*i*) conical pattern, of nominal working capacity 0·5, 1, 2 and 3 ml; and (*ii*) parallel pattern of nominal working capacity 0·5 and 1 ml. Some essential and recommended features are also specified for buckets, and for liners and pads used to accommodate the tubes in the buckets. H. P. PAGET

1415. **Alkoxyl and alkylimino group determination apparatus.** British Standards Institution (B.S. 1428: Part C 1: 1954, 10 pp.).—The design and dimensions of the following types of apparatus are described: (*i*) a simple form of micro-Zeisel apparatus suitable for teaching purposes and analysis; (*ii*) an alternative micro-Zeisel apparatus capable of more general application; and (*iii*) a robust form of Friedrich apparatus for the micro-determination of alkylimino groups.
H. P. PAGET

1416. **Simplified apparatus for quantitative hydrogenation.** R. L. Parrette (*Anal. Chem.*, 1954, **26** [1], 237–239).—Modifications of the apparatus by Gatterman and Wieland ("Laboratory Methods of Organic Chemistry," Macmillan & Co., London, 1943, p. 376) were made to overcome errors arising from the difficulties of (*i*) keeping the apparatus at constant temp. or pressure, (*ii*) bringing the sample into contact with the reduced catalyst and H without opening the apparatus to air and (*iii*) vigorously agitating the mixture of sample, catalyst, solvent and H without leakage of H. The standard deviation for a single determination, calculated from the results obtained by 3 operators on a series of duplicate determinations on 21 lots of 3 unsaturated resins, was $\pm$ 0·88 per cent.
G. P. COOK

1417. **New continuous extraction process for thermolabile substances.** M. Schirm (*Arch. Pharm., Berlin*, 1954, **287** [1], 46–49).—In order to minimise the exposure of the extract to heat, an evaporator consisting of a 3-bulb condenser (heated by circulating through the jacket a suitable vapour generated in a separate flask) is interposed between the extraction tube and the (unheated) flask for receiving the conc. extract. The middle bulb of the evaporator carries an additional tube leading direct into the receiving flask. The extractor (Soxhlet type without syphon) carries a side tube, with stopcock at the base, draining into a separating funnel that discharges through a U-tube into a tube connecting the receiving flask with the evaporator. The operation and construction are described and illustrated. P. S. ARUP

1418. **An improved form of micro azotometer.** F. R. Cropper (*Analyst*, 1954, **79**, 178–179).—An improved form of micro azotometer for use in the Dumas method for determination of N is described and illustrated. It avoids the use of a greased tap in contact with 50 per cent. KOH soln. with its possibility of leakage under reduced pressure. The

glass tap has been replaced by a horizontal connecting tube leading to a mercury seal and tap device. A. O. JONES

1419. **Method of measuring ultrafine glass fibres.** R. K. Ladisch, B. McQue and S. L. Knesbach (*Anal. Chem.*, 1954, **26** [2], 399–400).—Surface areas are calculated from a measurement of N adsorption by the method of Brunauer, Emmett and Teller (*J. Amer. Chem. Soc.*, 1938, **60**, 309). Values found can be used for the classification of these fibres. Small deviations in the average fibre diameter are readily detected as the surface area of a given weight increases inversely with decreasing fibre diameter. J. DAVIS

1420. **Simple photo-electric signalling device for use with chromatographic columns.** W. L. Porter (*Anal. Chem.*, 1954, **26** [2], 439).—The device indicates the approach of the end of a fraction. A light beam passes through the solvent just above the graduation marking the end vol. of the fraction to be cut. A glass float moving with the meniscus cuts the light beam, eventually causing a bell to ring. J. DAVIS

1421. **An automatic fraction collector for chromatography.** G. Brunisholz and A. Germano (*Helv. Chim. Acta*, 1954, **37** [1], 242–245).—A description is given of a pressure operated device that enables fractions of constant volume to be collected automatically. D. LIFF

1422. **Solvent tray and tray supports for one-dimension descending paper chromatography in glass cylinders.** W. L. Porter (*Anal. Chem.*, 1954, **26** [2], 439–440).—A stainless steel band expansion ring is inserted in a plain glass cylinder, the tray is placed in position and the bolts are fully tightened when the tray is level on the support bracket. Diagrams give the relevant dimensions of the parts. As the assembly does not rest on the bottom of the tank it is stable and the area under the tray is clear and unobstructed, troughs on each edge of the tray prevent the paper from touching the tray sides so preventing the solvent from rising by capillarity and a slot in the inner side of the trough allows accumulated solvent to return to the tray. J. DAVIS

1423. **Tank for 8 × 8-inch paper chromatograms.** L. C. Mitchell (*J. Ass. Off. Agric. Chem.*, 1953, **36** [4], 1187–1188).—The container illustrated is lined with blotting paper of which the bottom edge dips into the same mobile solvent as is used in the troughs. A. A. ELDRIDGE

1424. **A semi-automatic recording densitometer for use after paper-strip electrophoresis.** A. L. Latner (*J. Lab. Clin. Med.*, 1954, **43** [1], 157–164).—A scanning device has been constructed which operates in transmitted or reflected light. In reflected light the instrument covers ranges of protein concn. with an accuracy comparable to that attained by transmission. It also lends itself to completely automatic scanning and simultaneous area integration. N. E.

1425. **A vacuum vapour - liquid equilibrium still.** S. R. M. Ellis and B. A. Froome (*Chem. & Ind.*, 1954, [9], 237–240).—The new still is satisfactory at pressures of 50 to 760 mm of mercury, the max. pressure-drop throughout the apparatus being less than 1 mm. A modified device for mixing the condensed vapour and re-circulating liquid is described, and experimental details of operation of the still with a *n*-propanol and ethylbenzene binary system are given. M. TADMAN

See also Abstracts 1276, 1277, 1375.

Optical

1426. **Quantometry in 1952.** M. F. Hasler (*Spectrochim. Acta*, 1953, **6** [1], 69–79).—The Production Control Quantometer, made by Applied Research Laboratories, Glendale, California, is illustrated and described; comparisons are made of replicate analyses at different times with the same alloy samples. A method for preparing slag samples for analysis with the instrument is given, and the accuracy attainable is shown to depend mainly upon the limitations of sample preparation methods. E. J. H. BIRCH

1427. **A small adjustable X-ray crystal monochromator.** J. Fortey and E. Cohen (*J. Sci. Instrum.*, 1954, **31** [1], 11–13).—An X-ray monochromator has been designed for measuring X-ray scattering patterns from glassy substances. Parasitic and "white" radiations are suppressed and the strongest component of a multiply-reflected beam can be selected. The instrument is not suitable for use with elastically bent focusing crystals. G. SKIRROW

1428. **The application of the hollow cathode source to spectrographic analysis.** F. T. Birks (*Spectrochim. Acta*, 1954, **6** [2], 169–179).—A water-cooled hollow cathode for quant. spectrochemical analysis is described. The hollow cathode tube is arranged to permit rapid loading of routine samples. The effects of variations in current and in rare-gas pressure on the analytical results are examined. Typical detection limits for the halogens and the alkali metals are given; 5 μg of F as NaF is determined with a standard deviation of $\pm$ 12·4 per cent. The halogens can be detected in non-volatile organic matter without pre-treatment of the samples. The most sensitive F line is 7128·0 A. E. HAYES

1429. **Use of direct-reading spectrographic analysis in the aluminium industry.** J. Orsag (*Spectrochim. Acta*, 1953, **6** [1], 80–84).—A direct-reading spectrograph, made by the "Radio-Cinema" company under Péchiney licence, having two photomultiplier tubes (one for the base metal of the alloy and the other for moving to pre-determined lines of the spectrum) is described. The instrument has an integration time of $\simeq$ 0·5 sec. Examples are given of the effect of the type of graphite used for the electrodes, the width of the spark gap and the capacity of the spark system; a detailed method of use is given. For refined Al, in which the amount of Fe, Cu and Si is small, it is suggested that the spark generator should be replaced by an arc source, but this is less stable. A simplified apparatus for the analysis of Fe and Si only is mentioned. It is noted that analysis of Mg alloys is easier than that of Al, as both spark and arc excitation are more regular. E. J. H. BIRCH

1430. **A photo-electric spectrophotometer for the vacuum ultra-violet region.** V. J. Hammond and W. C. Price (*J. Sci. Instrum.*, 1954, **31** [3], 104–106).—In the instrument described, particular attention has been paid to overcoming difficulties

due to scattered light and the low reflecting power and rapid deterioration of aluminised surfaces. Light scattering is eliminated by vibrating the Littrow mirror about a horizontal axis while it scans by rotating about a vertical one. Thus the spectral image is alternated 10 times per sec. on and off the exit slit, the scattered light being unaffected. The instrument has a quant. limit in the region of 150 mμ. G. SKIRROW

1431. **Direct recording of Raman spectra.** J. Skinner (*Spectrochim. Acta*, 1953, **6** [1], 110–114).—The direct recording of Raman spectra by means of a photomultiplier tube is discussed. Reasonable reproducibility is attained for the weak lines of such a spectrum provided a high time-constant and a low scanning speed are used. E. J. H. BIRCH

1432. **A submersible photo-electric absorptiometer.** L. J. Scragg, R. Briggs and G. Knowles (*J. Sci. Instrum.*, 1954, **31** [3], 75–77).—The instrument described was designed for turbidity measurements in rivers. Transmitted light is received by a 20-element barrier-layer photo-cell while a second photo-cell compensates for variations in source brightness. The measuring head is connected by cable to a vacuum-tube voltmeter at the surface. The instrument has a range of 0·01 to 100 per cent. transmission and a maximum working depth of 100 feet. G. SKIRROW

1433. **An adaptation of the Beckman spectrophotometer for use as a fluorimeter.** R. V. Swann (*Analyst*, 1954, **79**, 176–178).—A detailed description is given of a system of combining the photo-cell portion of a Beckman spectrophotometer with the Spekker fluorimeter thus avoiding the use of the sensitive galvanometer of the other instrument which is so liable to vibration disturbances. A. O. JONES

1434. **Use of modulated light in photo-electric analysers for the determination of gas[es] in industrial control.** C. Cherrier, L. Verot and R. Wagner (*Spectrochim. Acta*, 1953, **6** [1], 87–94).—A (patented) apparatus is described in which visible or u.v. light from a mercury-vapour lamp modulated with a.c. passes partly through the gas to be analysed to one photo-electric cell and directly to another. These cells are mounted in opposition with a controlling potentiometer between them; their joint output at 100 cycles is amplified and fed to a recorder and a relay to operate alarms or valves if the amount of analysed component passes pre-set limits. The apparatus has been used with visible light for 0 to 1 per cent. of Cl in HCl, with u.v. light for up to 7 per cent. of SO_2 in SO_3 and with visible light for NO_2. With NO_2, the temp. of the gas is kept constant at 200° C. Humidity is measured with a sensitivity of 10 to 250 mg per cu. metre by passing the gas over oleum and measuring the absorption of the aerosol formed. E. J. H. BIRCH

1435. **Automatic servo-operated filter photometer.** J. M. Snodgrass, D. E. Carritt and W. S. Wooster (*Anal. Chem.*, 1954, **26** [1], 249–250).—A photometer designed for shipboard analysis is described. It operates on the double photo-cell principle, a servo motor driving the main slide wire and automatically eliminating lack of balance between the signals from the photo-cells. Monochromatic light is obtained by use of interference-type filters peaked at the desired wavelength. A standard deviation of 0·0008 is attained for an absorbancy of 0·332 at 696 mμ. G. P. COOK

Electrical

1436. **A simple thermionic vacuum gauge.** G. K. T. Conn and H. N. Daglish (*J. Sci. Instrum.*, 1954, **31** [3], 95–96).—The simply-constructed gauge described has linear characteristics in the region of 10^{-4} mm of Hg or less and a sensitivity of about 13 microamperes per μ pressure per mA anode current. G. SKIRROW

1437. **Application of the cathode-ray polarography to rotating platinum electrodes.** I. Shain and A. L. Crittenden (*Anal. Chem.*, 1954, **26** [2], 281–284).—A commercial cathode-ray oscillograph was modified to permit the observation of the current - voltage curves at rotated platinum electrodes in times comparable with those of the dropping-mercury electrode. The current flowing through the cell was measured by applying the voltage drop across the decade to the vertical amplifier of the oscillograph, while the voltage across the cell alone was applied to the horizontal amplifier. This potential was varied linearly with time by a mechanically driven potentiometer in place of the usual electronic sweep generators. The circuit is given with resistance values, etc. The polarographic reductions studied were: I′ in KCl, KNO_3 or H_2SO_4; IO_3^-; $[Fe(CN)_6]^{''''}$; Ag in KNO_3 - aq. NH_3; and hydroquinone in KCl (0·4 to 4·0 *M*). $E_{\frac{1}{2}}$ values are given for each of the reductions studied. The oxidation of $Fe^{\cdot\cdot}$ gave erratic results except in a limited concn. range. The relation between limiting current and concn. for the ranges studied was generally linear. B. LAMB

1438. **Rotating platinum electrode for amperometric titration of mercapto groups.** F. J. Herbert and J. R. Denson (*Anal. Chem.*, 1954, **26** [2], 440).—The electrode, which is made of borosilicate glass, consists of a stationary well and a tube with bell-shaped rotating top. A platinum wire is sealed into the side-arm and another, which extends to the outer edge of the bell, is sealed into the bottom of the electrode. Corks are used for bearings. Advantages include operation at variable speeds up to 1200 r.p.m. and lack of need for its insulation or removal from its operating position. J. DAVIS

1439. **Electronic method for bubble frequency measurement.** A. O. Newman and B. J. Lerner (*Anal. Chem.*, 1954, **26** [2], 417–418).—A mechanico-electronic method is described for measuring bubble frequencies of between 3·5 and 50 bubbles per sec. The bubble release "noise" impulse is picked up on a microphone, amplified and compared with a sine wave of known frequency on an oscilloscope screen. J. DAVIS

1440. **An electronic coulometer.** K. W. Kramer and R. B. Fischer (*Anal. Chem.*, 1954, **26** [2], 415–416).—A circuit diagram is given for a new type of electronic coulometer. The total number of discharges through a thyratron oscillator is proportional to the amount of current flowing through a resistor during the same period. The thyratron discharges are counted with a commercial scaling unit and mechanical register. J. DAVIS

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
atomic	at.
boiling-point	b.p.
British thermal unit	B.Th.U.
calculated	(calc.)
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
critical	crit.
crystalline, crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment, -al	expt.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
indefinite	indef.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim -um, -a	max.
melting-point	m.p.
microgram	μg
micro-litre	μl
micron	μ
milliampere	mA
milligram	mg
millilitre	ml
millimetre	mm
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
organic	org.
ounce	oz.
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	$n\lambda^{t}$
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]\lambda^{t}$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

Volume 1. No. 6, Abstracts 1176-1440 June, 1954

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: R. C. Chirnside. *Members:* B. S. Cooper, B. A. Ellis, D. C. Garratt, W. A. Waygood, I. D. P. Wootton.

President of the Society: D. W. Kent-Jones

Hon. Secretary of the Society: K. A. Williams

Secretary: Mrs. D. V. Hicks

Hon. Treasurer of the Society: J. H. Hamence

Editor: Norman Evers, B.Sc., Ph.D., F.R.I.C.

Assistant Editor: B. J. Walby, B.Sc.

CONTENTS

	Abstract
General Analytical Chemistry	1176
Inorganic Analysis	1198
Organic Analysis	1276
Biochemistry	
Blood, Bile, Urine, etc.	1311
Drugs	1339
Food	1354
Sanitation	1381
Agriculture and Plant Biochemistry	1389
General Technique and Laboratory Apparatus	
General	1410
Optical	1426
Electrical	1436

Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England. Communications to be addressed to the Editor, Norman Evers, 20, Eastcheap, London, E.C.3. Enquiries about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office